

(12)

(21) 2 315 137

(51) Int. Cl. 7: **C11D 17/02, C11D 1/14,
C11D 3/37, C11D 3/395**

(22) 04.08.2000

(30) 199 37 428.7 DE 07.08.1999

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(54) PASTILLES POUR LE NETTOYAGE

(54) CLEANING TABLETS

(57)

One or more polyalkylene glycols are used to improve the moisture stability of cleaning tablets and are present in cleaning tablets excluding tablets which contain (i) surfactant and builder particles coated with a polyethylene glycol having a molecular of 1,500 or which have been produced (ii) using 5 to 20% by weight of an amorphous overdried silicate, (iii) using 1 to 15% by weight of water or aqueous solutions or (iv) by compacting a particulate detergent composition with a binder distributed therein at a temperature of at least 28.degree.C, but below the melting point of the binder of 35 to 90.degree.C. In a process for producing a cleaning tablet, a particulate cleaning composition with one or more polyalkylene glycols distributed therein is compacted at a temperature below 28.degree.C. One or more cleaning tablets containing polyalkylene glycol may be combined with a pack accommodating the cleaning tablet(s), the pack having a water vapor transmission rate of 0.1 g/m2/day to less than 20 g/m2/day where it is stored at 23.degree.C/85% relative equilibrium humidity. The cleaning tablets are used for cleaning lavatories, descaling, cleaning hard surfaces, manual dishwashing, machine dishwashing, bleaching, stain removal, washing and/or water softening.

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(21) (A1) **2,315,137**
(22) 2000/08/04
(43) 2001/02/07

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(51) Int.Cl.⁷ C11D 17/02, C11D 3/395, C11D 3/37, C11D 1/14
(30) 1999/08/07 (199 37 428.7) DE
(54) **PASTILLES POUR LE NETTOYAGE**
(54) **CLEANING TABLETS**

(57) One or more polyalkylene glycols are used to improve the moisture stability of cleaning tablets and are present in cleaning tablets excluding tablets which contain (i) surfactant and builder particles coated with a polyethylene glycol having a molecular of 1,500 or which have been produced (ii) using 5 to 20% by weight of an amorphous overdried silicate, (iii) using 1 to 15% by weight of water or aqueous solutions or (iv) by compacting a particulate detergent composition with a binder distributed therein at a temperature of at least 28 °C, but below the melting point of the binder of 35 to 90 °C. In a process for producing a cleaning tablet, a particulate cleaning composition with one or more polyalkylene glycols distributed therein is compacted at a temperature below 28 °C. One or more cleaning tablets containing polyalkylene glycol may be combined with a pack accommodating the cleaning tablet(s), the pack having a water vapor transmission rate of 0.1 g/m²/day to less than 20 g/m²/day where it is stored at 23°C/85% relative equilibrium humidity. The cleaning tablets are used for cleaning lavatories, descaling, cleaning hard surfaces, manual dishwashing, machine dishwashing, bleaching, stain removal, washing and/or water softening.



Abstract

One or more polyalkylene glycols are used to improve the moisture stability of cleaning tablets and are present in cleaning tablets excluding tablets which contain (i) surfactant and builder particles coated with a polyethylene glycol having a molecular of 1,500 or which have been produced (ii) using 5 to 20% by weight of an amorphous overdried silicate, (iii) using 1 to 15% by weight of water or aqueous solutions or (iv) by compacting a particulate detergent composition with a binder distributed therein at a temperature of at least 28°C, but below the melting point of the binder of 35 to 90°C. In a process for producing a cleaning tablet, a particulate cleaning composition with one or more polyalkylene glycols distributed therein is compacted at a temperature below 28°C. One or more cleaning tablets containing polyalkylene glycol may be combined with a pack accommodating the cleaning tablet(s), the pack having a water vapor transmission rate of 0.1 g/m²/day to less than 20 g/m²/day where it is stored at 23°C/85% relative equilibrium humidity. The cleaning tablets are used for cleaning lavatories, descaling, cleaning hard surfaces, manual dishwashing, machine dishwashing, bleaching, stain removal, washing and/or water softening.

CLEANING TABLETS

Field of the Invention

This invention relates to the use of polyalkylene glycols for improving the moisture stability of cleaning tablets and to certain cleaning tablets with improved moisture stability which contain polyalkylene glycols. In the context of the invention, cleaning tablets include, for example, tablets for
5 washing laundry, tablets for machine or manual dishwashing or for cleaning of hard surfaces, bleach tablets for use in washing or dishwashing machines, water softening tablets, stain remover tablets and lavatory cleaning tablets.

Background of the Invention

10 Cleaning tablets of the product classes mentioned are widely described in the prior art literature and are enjoying increasing popularity among consumers by virtue of the fact that they are easy to dose. Tabletted detergents have a number of advantages over powder-form or liquid products: they are easier to dose and handle and, by virtue of their
15 compact structure, have advantages in regard to storage and transportation. Accordingly, there is an extremely broad prior art on the subject of cleaning tablets which is also reflected in extensive patent literature.

Lavatory cleaners in tablet form which contain acids and surfactants
20 are well known. To accelerate the dissolution and distribution of the active substances in the lavatory bowl, lavatory cleaner tablets preferably contain sodium carbonate and/or sodium bicarbonate as an effervescent component.

It is known that corresponding formulations are extremely sensitive
25 to moisture so that expensive packs impermeable to water vapor and/or additional drying agents are required to guarantee stability in storage.

EP 0 522 766 A (*Unilever*) discloses tablets of a compacted particulate detergent component containing surfactants, builders and

optionally other detergent ingredients which, in at least one discrete region, only contain particles at least 200 μm in size with a size range covering no more than 700 μm and which contain (i) surfactant and builder particles coated with a polyethylene glycol having a molecular weight of 1500.

5 **DE 197 09 41** (*Henkel KGaA*) discloses a process for the production of detergent tablets containing surfactants, builders and optionally other detergent ingredients by tableting a particulate detergent composition, in which 0.5 to 10% by weight of polyethylene glycol and (ii) 5 to 20% by weight of an amorphous overdried silicate and (iii) 1 to 15% by weight of
10 water or aqueous solutions, based on the weight of the tablet formed, are used to produce the tablets.

EP 0 711 828 A (*Unilever*) discloses a process for the production of detergent tablets containing surfactants builders and optionally other detergent ingredients (iv) by compacting a particulate detergent
15 composition with a binder distributed therein at a temperature of at least 28°C, but below the melting point of the binder of 35 to 90°C. The binder may be selected inter alia from polyethylene glycols, for example polyethylene glycols with a molecular weight of 1,500, 4,000 or 6,000.

 However, there is nothing in the prior art to suggest that
20 polyethylene glycols would be effective in improving the moisture stability of cleaning tablets.

 The problem addressed by the present invention was to improve the moisture stability of cleaning tablets.

Summary of the Invention

25 The present invention relates to the use of one or more polyalkylene glycols for improving the moisture stability of cleaning tablets.

 In a second embodiment, the present invention relates to a cleaning tablet containing one or more polyalkylene glycols, excluding tablets which contain

- i) surfactant and builder particles coated with a polyethylene glycol having a molecular weight of 1,500 or which have been produced
- ii) using 5 to 20% by weight of an amorphous overdried silicate,
- 5 iii) using 1 to 15% by weight of water or aqueous solutions or
- iv) by compacting a particulate detergent composition with a binder distributed therein at a temperature of at least 28°C, but below the melting point of the binder of 35 to 90°C.

In a third embodiment, the present invention relates to a process for
10 the production of a cleaning tablet by compacting a particulate detergent composition with one or more polyalkylene glycols distributed therein at a temperature below 28°C.

In a fourth embodiment, the present invention relates to a combination of one or more cleaning tablets containing polyalkylene glycol and a
15 pack containing the cleaning tablet(s), the pack having a water vapor transmission rate of 0.1 g/m²/day to less than 20 g/m²/day where it is stored at 23°C and at a relative equilibrium humidity of 85%.

In a fifth embodiment, the present invention relates to the use of one or more cleaning tablets according to the invention for cleaning toilets, descaling, cleaning hard surfaces, manual dishwashing, machine
20 dishwashing, bleaching, stain removal, washing and/or water softening. The cleaning tablets are preferably used for cleaning flush toilets, more particularly in the region of the water standing in the bottom of the lavatory bowl, for descaling domestic appliances, more particularly coffee machines and kettles, for cleaning hard surfaces in the home, more particularly floors
25 and surfaces in kitchens and bathrooms or toilets, for manual dishwashing, for machine dishwashing, for bleaching, stain removal or washing textile articles and surfaces, more particularly clothing, table linen, bed linen, upholstery, curtains and carpets or carpeting and in the interior of

automobiles and/or for softening water in washing machines.

One particular advantage of the invention is that the improvement in moisture stability is not achieved at the expense of other properties of the cleaning tablets, i.e. the other properties are not adversely affected by the polyalkylene glycols. This is also apparent from the following Examples.

Detailed Description of the Invention

The following description of the invention - unless otherwise specifically stated - applies to all embodiments of the invention, i.e. for example both to the use according to the invention and to the cleaning tablet according to the invention, even if each embodiment of the invention is not expressly mentioned.

Molecular weights are expressed as "unitless" relative molecular weights, the molecular weights of polymers, more particularly the molecular weights of the higher polyalkylene glycols, representing average relative molecular weights.

Unless otherwise specifically indicated, quantities and contents are expressed in % by weight, based on the cleaning tablet. In this connection, variously preferred quantity ranges, such as "preferably 0.1 to 10% by weight, more preferably 1 to 5% by weight", simultaneously signify preferred upper and lower limits, i.e. "preferably at least 0.1% by weight, more preferably at least 1% by weight but no more than 10% by weight and more particularly no more than 5% by weight" and, accordingly, also mean that the quantity ranges of 0.1 to 5% by weight and 1 to 10% by weight are preferred to 0.1 to 10% by weight.

Substances which also serve as ingredients of cosmetic preparations may be referred to in the following by their names under the INCI nomenclature (INCI = *International Nomenclature of Cosmetic Ingredients*). Chemical compounds bear an INCI name in English while vegetable ingredients are all referred to by their Latin names according to

Linné, so-called trivial names such as "water", "honey" or "sea salt" also being shown in Latin. The INCI names can be found in the **International Cosmetic Ingredient Dictionary and Handbook - 7th Edition (1997)** which is published by the **Cosmetic, Toiletry and Fragrance Association (CTFA), 1101 17th Street, NW, Suite 300, Washington, DC 20036, USA** and which contains more than 9,000 INCI names and references to more than 37,000 commercial names and technical names, including the associated distributors from more than 31 countries. The *International Cosmetic Ingredient Dictionary and Handbook* assigns the ingredients to one or more chemical classes, for example *Polymeric Ethers*, and one or more functions, for example *Surfactants - Cleansing agents*, which in turn are explained in detail and to which reference may also be made in the following.

15 Polyalkylene glycols

Polyalkylene glycols (polyglycols, polyglycol ethers; INCI Chemical Class: Polymeric Ethers) are known, predominantly linear, but occasionally branched polyethers which are hydroxy-terminated polymers. The relatively high molecular weight polyalkylene glycols are polymolecular, i.e. they consist of "collectives" of macromolecules with various molecular weights.

According to the invention, polyalkylene glycols are used in a quantity of normally 0.1 to 20% by weight, preferably 0.5 to 10% by weight, more preferably 1 to 7% by weight and most preferably 2 to 5% by weight.

25 The quantity of polyalkylene glycols present in the cleaning tablet is preferably selected so that it is completely soluble in the quantity of water taken up by the cleaning tablet - for more than one cleaning tablet to be taken up by the quantity of water in the corresponding partial quantity of water. The maximum soluble quantity is determined both by the solubility

of the polyalkylene glycol in water and by the said quantity or partial quantity of water which is dependent upon the particular application of the cleaning tablet. Both values are either known or can be determined by simple tests.

- 5 According to the invention, linear or branched, more particularly linear, polyalkylene glycols with the following general formula:



- 10 in which R represents $(\text{CH}_2)_2$, $\text{CH}_2\text{CH}(\text{CH}_3)$ and/or $(\text{CH}_2)_4$ and n has a value of 2 to more than 100,000 and which are obtainable by ring-opening polymerization of ethylene oxide, propylene oxide and/or tetrahydrofuran, are preferred. More particularly, these polyalkylene glycols are polyethylene glycols with $\text{R} = (\text{CH}_2)_2$, polypropylene glycols with $\text{R} = \text{CH}_2\text{CH}(\text{CH}_3)$, polytetrahydrofurans with $\text{R} = (\text{CH}_2)_4$ and copolymers of ethylene oxide,
15 propylene oxide and/or tetrahydrofuran.

- In one preferred embodiment of the invention, preferred polyalkylene glycols have a melting point above the temperature prevailing during production of the cleaning tablet, preferably above a room temperature of about 21°C , more preferably above 23°C and most preferably at least
20 28°C . The melting point of homologous homopolymeric polyalkylene glycols generally increases with increasing molecular weight and narrowing molecular weight distribution. In addition, the melting point of copolymeric polyalkylene glycols generally increases with increasing oxygen content - in the case of ethylene oxide/propylene oxide copolymers for example,
25 generally with increasing polyethylene glycol content. Finally, the melting point of the polypropylene glycols generally increases with increasing tacticity (stereoregularity).

Polyethylene glycols

According to the invention, polyethylene glycols (PEGs) with an average relative molecular weight of 800 to 100,000, normally 1,000 to 80,000, preferably 1,500 to 70,000 and more preferably 2,000 to 60,000 are suitable.

Low molecular weight PEGs with molecular weights below 800 are clear, substantially colorless liquids and are therefore less suitable for the purposes of the invention. Beyond a molecular weight of about 800, PEGs become partly crystalline solids. With increasing molecular weight, PEGs change first into soft waxes at molecular weights of about 1,000 to 2,000 and then into hard waxes at molecular weights of up to about 20,000 and higher. Finally, high molecular weight PEGs with molecular weights above 100,000 are hard thermoplastics and, accordingly, are unsuitable for the purposes of the invention.

One particularly advantageous embodiment of the present invention is characterized by the use of one or more polyethylene glycols with a molecular weight of at least 3,000, preferably in the range from 4,000 to 50,000, more preferably in the range from 6,000 to 40,000, most preferably in the range from 8,000 to 30,000 and, in one most particularly preferred embodiment, in the range from 10,000 to 20,000. Cleaning tablets according to this embodiment are particularly moisture-stable, their moisture stability being significantly improved by comparison with cleaning tablets containing polyethylene glycol with a molecular weight of less than 3,000.

There are various nomenclatures for polyethylene glycols which can lead to confusion. Technically, it is standard practice to show the average relative molecular weight after the initials "PEG", so that "PEG 200" characterizes a polyethylene glycol having a relative molecular weight of ca. 190 to ca. 210.

Under the INCI nomenclature, the initials PEG are followed by a hyphen which in turn is directly followed by a number which corresponds to the number n in the above general formula, the three zeros "000" in multiples of 1,000 being replaced by the letter "M" so that, for example, PEG-7M stands for a PEG having an average n value of 7,000.

Commercially obtainable polyethylene glycols with a molecular weight below 3,000 are, for example, PEG 800/PEG-18, PEG-20, PEG 1000, PEG 1200, PEG 1500/PEG-32, PEG-40, PEG 2000, PEG-55 and PEG-60, the names under the two nomenclatures for corresponding polyethylene glycols being separated from one another by the symbol "/".

Commercially obtainable polyethylene glycols with a molecular weight of 3,000 to 88,000 are, for example, PEG 3000, PEG 3350/PEG-75, PEG 4000/PEG-90, PEG 4500/PEG-100, PEG 4600, PEG 6000/PEG-135, PEG 7000, PEG-150, PEG 8000/PEG-180, PEG 9000/PEG-200, PEG 10000/PEG-240, PEG 12000, PEG 14000, PEG 15000/PEG-350, PEG-400, PEG 20000, PEG 35000, PEG 50000 and PEG-2M, the names under the two nomenclatures for corresponding polyethylene glycols being separated from one another by the symbol "/".

The commercially obtainable polyethylene glycols are available, for example, under the names of Carbowax® 8000 (*Union Carbide*), Emkapol® 6000 and Renex® PEG 3350 (*ICI*), Lipoxol® (*DEA*), Polyglykol® E 4500 (*Dow*), Pluracol® E8000, Puriol® E12000 and Lutrol® E4000 (*BASF*) and the corresponding trade names with other numbers which represent the molecular weights of the polyethylene glycol. Reference sources for the polyethylene glycols with INCI names also serving as cosmetic ingredients can be found in the *International Cosmetic Ingredient Dictionary and Handbook*. The *Clariant* organization also markets polyethylene glycols, for example PEG 10000 to PEG 35000.

Polypropylene glycols

Polypropylene glycols (PPGs) are clear, substantially colorless liquids or amorphous or crystalline solids covering a broad molecular weight range, the liquids being less suitable for the purposes of the present invention. The INCI nomenclature mentioned above is also used analogously for naming polypropylene glycols.

Liquid viscous polypropylene glycols usually have molecular weights of 250 (PPG-4) to 4,000 (PPG-69); low molecular weight representatives are miscible with water while relatively high molecular weight PPGs are poorly soluble in water. The polypropylene glycols are formed by ring opening polymerization of propylene oxide. They can be produced as amorphous or stereoregular polymers, tacticity (stereoregularity) leading to the preferred crystalline PPGs.

According to the invention, the molecular weights of the polypropylene glycols are normally in the range from ca. 2,000 to 100,000, preferably in the range from 4,000 to 50,000, more preferably in the range from 6,000 to 40,000, most preferably in the range from 8,000 to 30,000 and, in one most particularly preferred embodiment, in the range from 10,000 to 20,000.

Polypropylene glycols are usually obtainable as di- and trihydroxy-PPGs in a broad range of molecular weights. The third hydroxy group emanates from the polymerization initiator where glycerol, for example, is used as initiator for polypropylene glycols of which the three hydroxy groups react in the polymerization and thus lead to branched trihydroxy-PPGs.

Polytetrahydrofurans

The polytetrahydrofurans (PTHFs) are also known as tetramethylene glycols, polytetramethylene glycol ethers or polytetramethylene oxides and

are polyalkylene ethers obtainable by cationic polymerization (ring opening polymerization) of tetrahydrofuran at temperatures below 83°C.

PTHF's are strictly linear polyether diols which are industrially produced using fuming nitric acid or fluorosulfuric acid as catalysts.

- 5 According to the invention, the molecular weights of the PTHFs, which can reach values of up to several million, are normally in the range from about 650 to 100,000, preferably in the range from 1,000 to 50,000, more preferably in the range from 1,400 to 30,000, most preferably in the range from 2,900 to 20,000 and, in one most particularly preferred embodiment,
10 in the range from 4,500 to 10,000.

- PTHF's are liquids or low-melting, normally crystalline solids at room temperature. The consistency of PTHFs increases with increasing molecular weight from oily through wax-like to solid. Amorphous PTHFs with molecular weights above 100,000 are rubber-like products. Partly
15 crystalline PTHFs melt at around 43°C. Low molecular weight PTHFs are soluble in water.

- Polytetrahydrofurans with molecular weights of 650, 1,000, 1,400, 2,000, 2,900 and 4,500, for example, are commercially obtainable. The commercially obtainable polytetrahydrofurans are available, for example,
20 under the names of Polytetrahydrofuran 650 or PolyTHF® 4500 (BASF), Terathane® 2900 and Teracol® 1000 (Du Pont) and Polymeg® 2000 (Quaker Oats) and the corresponding trade names with other numbers which represent the molecular weights of the polyethylene glycol.

25 Copolymers

The copolymers are preferably statistical copolymers and, more particularly, block copolymers of ethylene and propylene oxide, ethylene oxide and tetrahydrofuran, propylene oxide and tetrahydrofuran or ethylene oxide, propylene oxide and tetrahydrofuran, preferably block copolymers of

ethylene and propylene oxide and more preferably block copolymers of ethylene and propylene oxide. According to the invention, the molecular weights of the copolymers are normally in the range from about 2,000 to 100,000, preferably in the range from 3,000 to 50,000, more preferably in the range from 4,000 to 40,000, most preferably in the range from 6,000 to 30,000 and, in one most particularly preferred embodiment, in the range from 8,000 to 20,000.

According to the invention, preferred statistical copolymers of *a* ethylene and *b* propylene oxide units are, for example, the following copolymers (molecular weight) named as PEG/PPG-*a/b* according to the *International Cosmetic Ingredient Dictionary and Handbook*, *a* and *b* representing mean values: PEG/PPG-125/30 Copolymer (7300), PEG/PPG-150/30 Copolymer (8400) and PEG/PPG-300/55 Copolymer (16400).

According to the invention, preferred block copolymers of ethylene and propylene oxide correspond to the formula $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_y(\text{CH}_2\text{CH}_2\text{O})_z\text{H}$, in which *x* and *x'* stand for mean values of 2 to 130 while *z* stands for mean values of 15 to 67, and are referred to by the International non-proprietary name of *poloxamer* which is also used in the *International Cosmetic Ingredient Dictionary and Handbook*. Every poloxamer is characterized by a three-digit number. The first two digits multiplied by 100 indicate the average molecular weight of the polypropylene glycol component while the last digit multiplied by 10 indicates the polyethylene glycol content in % by weight which is between 10 and 80% by weight, preferably at least 30% by weight, more preferably at least 40% by weight, most preferably at least 50% by weight and, in one most particularly preferred embodiment, at least 60% by weight, for example 70 or 80% by weight. The poloxamers are produced in two stages, propylene oxide being added under control onto propylene glycol in

the first stage and the polypropylene glycol block obtained being enclosed by two polyethylene glycol blocks by subsequent addition of ethylene oxide.

Particularly preferred block copolymers are, for example, the following poloxamer types (x, y, x'; molecular weight; in some cases melting point): poloxamer 185 (19, 30, 19; 3500; 27), poloxamer 215 (24, 35, 24; 4150; 34), poloxamer 234 (22, 39, 22; 4200), poloxamer 284 (21, 47, 21; 4600), poloxamer 235 (27, 29, 27; 4650; 29), poloxamer 333 (20, 54, 20; 4900; 30), poloxamer 108 (46, 16, 46; 4950; 48), poloxamer 402 (13, 67, 13; 5000; 20), poloxamer 403 (21, 67, 21; 5750; 31), poloxamer 334 (31, 54, 31; 5900; 32), poloxamer 335 (38, 54, 38; 6500; 30), poloxamer 217 (52, 35, 52; 6600; 48), poloxamer 237 (62, 39, 62; 7700; 49), poloxamer 188 (75, 30, 75; 8350; 52), poloxamer 238 (97, 39, 97; 11400; 54), poloxamer 407 (98, 67, 98; 12600; 56), poloxamer 288 (122, 47, 122; 13000; 58) and poloxamer 338 (128, 54, 128; 14600; 57).

The poloxamers are commercially obtainable under the names of Pluronic® and Synperonic® PE followed by the letter L, P or F and a two-digit or three-digit number. The last digit is identical with the last digit of the poloxamer nomenclature and the preceding single- or two-digit numbers multiplied by 300 indicate the approximate molecular weight of the polypropylene glycol component and, multiplied by 3, approximately the number formed from the first two digits of the poloxamer nomenclature number, i.e. 3, 4, 6, 7, 8, 9, 10 and 12 correspond in that order to the 2-digit numbers 10, 12, 18, 21, 23, 28, 33 and 40 at the beginning of the number under the poloxamer nomenclature. The letters distinguish between liquid (L), paste-form (P) and solid (F) poloxamers. Thus, poloxamer 238, for example, is obtainable as Pluronic® F 88 and Synperonic® PE F 88.

Another class of suitable block copolymers of ethylene and propylene oxide correspond to the formula

HO(CH(CH₃)CH₂O)_y(CH₂CH₂O)_x(CH₂CH(CH₃)O)_yH. Here, one polyethylene glycol block is enclosed by two polypropylene glycol blocks whereas, in the case of the poloxamers, one polypropylene glycol block is enclosed by two polyethylene glycol blocks. Production is again carried out in two stages, ethylene oxide being added under control onto ethylene glycol in the first stage and the polyethylene glycol block obtained being enclosed by two polypropylene glycol blocks by subsequent addition of propylene oxide.

These block copolymers like the poloxamers are commercially obtainable under the name of Pluronic® (BASF) followed by an alpha-numeric code of three digits and the letter R between the second and third digits. The meaning of the digits is identical with their meaning under the poloxamer nomenclature. The letter R (reverse) between the second and third digits indicates the inverted structure compared with the poloxamers. Preferred representatives of this class are the following Pluronic® types (molecular weight; melting point): Pluronic® 17R4 (2650; 18), Pluronic® 22R4 (3350; 24), Pluronic® 25R4 (3600; 25), Pluronic® 31R4 (4150; 24), Pluronic® 25R5 (4250; 30), Pluronic® 10R8 (4550; 46), Pluronic® 17R8 (7000; 53), Pluronic® 25R8 (8550; 54).

20

Other ingredients

Besides the polyalkylene glycols crucial to the invention, the cleaning tablets contain one or more other ingredients typical of detergents or rather cleaning tablets. The nature and quantity of the other ingredient(s) is/are determined in the usual way by the application envisaged for the cleaning tablet.

25

The other ingredients perform one or more primary functions and/or one or more secondary functions. The primary functions are concerned with the actual cleaning or washing effect of the cleaning tablet and its in-

use handling behavior, for example its disintegration properties. The secondary functions are concerned with the production of the cleaning tablet and its handling behavior in production, for example its fracture resistance. Other ingredients with secondary functions are also known as
5 tableting aids or tablet auxiliaries. A clear division into other ingredients with a purely primary function and those with a purely secondary function is not always possible because primary and secondary functions are often fulfilled at the same time. More particularly, the other ingredients with secondary functions may optionally combine several properties.

10 Other ingredients of importance by virtue of their primary function are disintegration aids, surfactants, bleaching agents and builders and also corrosion inhibitors, soil release compounds, enzymes, soil repellents, optical brighteners, dyes and perfumes and antimicrobial agents. Other ingredients of importance by virtue of their secondary function are fillers,
15 separating agents or lubricants, binders and powdering materials. These other ingredients are described in the following.

The expert will have no difficulty in selecting the individual components and their quantities according to the application envisaged for the cleaning tablets. For example, a heavy-duty detergent tablet will
20 contain relatively large quantities of surfactant(s) whereas a bleaching tablet may even contain no surfactant at all.

Disintegration aids

In order to facilitate the disintegration of heavily cleaning compacted
25 tablets, disintegration aids, so-called tablet disintegrators, may be incorporated in them to shorten their disintegration times. According to Römpp (9th Edition, Vol. 6, page 4440) and Voigt "*Lehrbuch der pharmazeutischen Technologie*" (6th Edition, 1987, pages 182-184), tablet disintegrators or disintegration accelerators are auxiliaries which

promote the rapid disintegration of tablets in water or gastric juices and the release of the pharmaceuticals in an absorbable form.

These substances, which are also known as "disintegrators" by virtue of their effect, are capable of undergoing an increase in volume on contact with water so that, on the one hand, their own volume is increased (swelling) and, on the other hand, a pressure can be generated through the release of gases which causes the tablet to disintegrate into relatively small particles. So-called "effervescent systems" are also often used as disintegration-promoting systems in cleaning tablets. Well-known effervescent systems are carbonate/citric acid systems. Swelling disintegration aids are, for example, synthetic polymers, such as polyvinyl pyrrolidone (PVP), or natural polymers and modified natural substances, such as cellulose and starch and derivatives thereof, alginates or casein derivatives.

15 *Effervescent systems*

An effervescent system consists of a combination of two or more substances which release a gas, such as carbon dioxide or oxygen, on contact with water. Preferred effervescent systems consist of one or more acidic components and one or more carbon dioxide sources.

Suitable acidic components are, for example, organic acids, more particularly oligocarboxylic acids optionally containing hydroxy groups, such as the di- and tricarboxylic acids, for example succinic acid, oleic acid, glutaric acid, adipic acid, tartaric acid and, more particularly, citric acid, and acidic salts of polybasic inorganic or organic acids, for example potassium dihydrogen phosphate or sodium hydrogen sulfate, and amidosulfuric acid ($\text{H}_2\text{N SO}_2 \text{ OH}$; formerly: amidosulfonic acid, sulfamic acid). Particularly suitable CO_2 -releasing components are the salts of carbonic acid, i.e. carbonates and hydrogen carbonates and mixtures thereof which are used, above all, as alkali metal and alkaline earth metal salts.

Particularly preferred acidic components are amidosulfuric acid, citric acid and sodium hydrogen sulfate and mixtures thereof. Preferred mixtures consist of amidosulfuric acid and citric acid, preferably in a ratio by weight of amidosulfuric acid to citric acid of 100:1 to 1:100, more particularly 50:1 to 1:20, more preferably 20:1 to 1:10 and most preferably 13:1 to 10:1 or 2:1 to 1:2, for example 12:1 or 11:1 or 1:1. The mixtures of amidosulfuric acid and citric acid are preferably used as the sole acidic component of the effervescent system, although they may also be combined with sodium hydrogen carbonate and/or one or more other acid components.

Particularly preferred CO₂ components are sodium carbonate (soda) and sodium hydrogen carbonate (sodium bicarbonate) and mixtures of sodium carbonate and sodium hydrogen carbonate, more particularly sodium carbonate and mixtures of sodium carbonate and sodium hydrogen carbonate. Mixtures of sodium carbonate and sodium hydrogen carbonate normally have a ratio by weight of sodium hydrogen carbonate to sodium carbonate of 20:1 to 1:10, more particularly 10:1 to 1:1, more preferably 5:1 to 3:1 and most preferably 5:1 to 4:1, for example 3.6:1, 4.4:1 or 4.6:1.

The higher the hydrogen carbonate content of the CO₂ component and/or the content of an acid or CO₂ component or effervescent system as a whole, the more vigorously the effervescent system effervesces or foams and the more quickly the cleaning tablets usually decompose.

The choice of the content of acid and CO₂ component(s) also has to take into account the pH value which is supposed to be established in the use of the cleaning tablets. Thus, descaling tablets or lavatory cleaner tablets normally contain an excess of acid in order to guarantee sufficient acidity for the cleaning effect. For a tablet suitable for manual dishwashing, for example, a 10% by weight aqueous solution of the cleaning tablet may advantageously have a pH value below 7 and, more particularly, in the

range from 3 to 6. By contrast, an excess of CO₂ component may be selected, for example, for a multipurpose cleaning tablet in order to enable an alkaline cleaning solution sufficient for the desired cleaning effect to be obtained through dissolution of the cleaning tablet (for example a pH in the
5 range from 8 to 11).

The cleaning tablet contains an effervescent system in a quantity of normally 1 to 99.9% by weight, preferably 10 to 99% by weight and more preferably 20 to 98% by weight. The moisture-stabilizing effect of the alkylene polyglycols according to the invention is particularly advantageous
10 in effervescent and, more particularly, highly effervescent cleaning tablets.

In one preferred embodiment of the invention, the cleaning tablet contains an effervescent system in a quantity of at least 50% by weight, preferably at least 60% by weight, more preferably 70 to 97% by weight, most preferably 80 to 96% by weight and, in one most particularly preferred
15 embodiment, 85 to 95% by weight. Cleaning tablets corresponding to this preferred embodiment contain large amounts of acid and CO₂ component and/or an excess of acid or CO₂ component and are therefore suitable for applications where vigorous effervescence or foaming and/or high acidity or alkalinity is required, more particularly as cleaning tablets for flush toilets
20 (lavatory cleaner tablets) for the acidic cleaning of flush toilets and as descaling tablets (descaler tablet) for acidic descaling.

A cleaning tablet suitable for use as a manual dishwashing detergent may contain the effervescent system in a quantity of, for example, 20 to 70% by weight, preferably 25 to 60% by weight and more
25 preferably 28 to 55% by weight.

In embodiments of the present invention particularly suitable as laundry detergents and/or machine dishwashing detergents, however, the cleaning tablet is not an "effervescent tablet", i.e. is free from acid or CO₂ components, preferably free from acids, more particularly free from

oligomeric oligocarboxylic acids and more preferably free from citric acid.

Swelling disintegration aids

Instead of or in addition to an effervescent system, the cleaning
5 tablets may contain one or more swelling disintegration aids, normally in a
quantity of 0.5 to 10% by weight, preferably in a quantity of 3 to 7% by
weight and more preferably in a quantity of 4 to 6% by weight.

According to the invention, preferred swelling disintegrators are
cellulose-based disintegrators, so that preferred detergent tablets contain a
10 cellulose-based disintegrator in quantities of 0.5 to 10% by weight,
preferably 3 to 7% by weight and more preferably 4 to 6% by weight. Pure
cellulose has the formal empirical composition $(C_6H_{10}O_5)_n$ and, formally, is
a β -1,4-polyacetal of cellobiose which, in turn, is made up of two molecules
of glucose. Suitable celluloses consist of ca. 500 to 5000 glucose units
15 and, accordingly, have average molecular weights of 50,000 to 500,000.
According to the invention, cellulose derivatives obtainable from cellulose
by polymer-analog reactions may also be used as cellulose-based
disintegrators. These chemically modified celluloses include, for example,
products of esterification or etherification reactions in which hydroxy
20 hydrogen atoms have been substituted. However, celluloses in which the
hydroxy groups have been replaced by functional groups that are not
attached by an oxygen atom may also be used as cellulose derivatives.
The group of cellulose derivatives includes, for example, alkali metal
celluloses, carboxymethyl cellulose (CMC), cellulose esters and ethers and
25 aminocelluloses.

The cellulose derivatives mentioned are preferably not used on their
own, but rather in the form of a mixture with cellulose as cellulose-based
disintegrators. The content of cellulose derivatives in mixtures such as
these is preferably below 50% by weight and more preferably below 20%

by weight, based on the cellulose-based disintegrator. In one particularly preferred embodiment, pure cellulose free from cellulose derivatives is used as the cellulose-based disintegrator.

The cellulose used as disintegration aid is preferably not used in fine-particle form, but is converted into a coarser form, for example by granulation or compacting, before it is added to and mixed with the premixes to be tableted. Detergent tablets which contain granular or optionally co-granulated disintegrators are described in German patent applications **DE 197 09 991** (Stefan Herzog) and **DE 197 10 254** (Henkel) and in International patent application **WO 98/40463** (Henkel). Further particulars of the production of granulated, compacted or co-granulated cellulose disintegrators can also be found in these patent applications. The particle sizes of such disintegration aids are mostly above 200 μm , preferably at least 90% by weight of the particles being between 300 and 1600 μm in size and, more particularly, between 400 and 1200 μm in size. According to the invention, the above-described relatively coarse-particle cellulose-based disintegrators described in detail in the cited patent applications are preferably used as disintegration aids and are commercially obtainable, for example under the name of Arbocel® TF-30-HG from Rettenmaier.

Microcrystalline cellulose may be used as another cellulose-based disintegration aid or as part of such a component. This microcrystalline cellulose is obtained by partial hydrolysis of celluloses under conditions which only attack and completely dissolve the amorphous regions (ca. 30% of the total cellulose mass) of the celluloses, but leave the crystalline regions (ca. 70%) undamaged. Subsequent de-aggregation of the microfine celluloses formed by hydrolysis provides the microcrystalline celluloses which have primary particle sizes of ca. 5 μm and which can be compacted, for example, to granules with a mean particle size of 200 μm .

In one particular embodiment of the present invention particularly suitable as laundry and/or dishwasher detergents, preferred cleaning tablets contain one or more disintegration aids, preferably a swelling disintegration aid, more particularly based on cellulose, preferably in
5 granular, cogranulated or compacted form, in quantities of 0.5 to 10% by weight, preferably in quantities of 3 to 7% by weight and more preferably in quantities of 4 to 6% by weight, based on tablet weight.

Surfactants

10 Preferred cleaning tablets additionally contain one or more surfactants.

To develop their cleaning performance, the cleaning tablets according to the invention may contain surface-active compounds from the group of anionic, nonionic, zwitterionic and cationic surfactants, anionic
15 surfactants being distinctly preferred for economic reasons and for their performance spectrum.

The surfactant content of manual dishwashing tablets is normally between 10 and 40% by weight, preferably between 12.5 and 30% by weight and more preferably between 15 and 25% by weight whereas
20 machine dishwashing tablets normally contain between 0.1 and 10% by weight, preferably between 0.5 and 7.5% by weight and more preferably between 1 and 5% by weight. Tablets for cleaning hard surfaces (multipurpose cleaning tablets) may have the above-mentioned surfactant contents of up to and over 10% by weight, depending on their formulation.

25 Lavatory cleaning tablets usually contain up to 5% by weight of surfactants, preferably from 0.1 to 3% by weight, more preferably from 0.3 to 2% by weight and most preferably from 0.5 to 1% by weight. Bleach tablets and water softening tablets are normally free from surfactants.

Anionic surfactants

Suitable anionic surfactants are, for example, those of the sulfonate and sulfate type. Suitable surfactants of the sulfonate type are preferably C₉₋₁₃ alkyl benzenesulfonates, olefin sulfonates, i.e. mixtures of alkene and hydroxyalkane sulfonates, and the disulfonates obtained, for example, from C₁₂₋₁₈ monoolefins with an internal or terminal double bond by sulfonation with gaseous sulfur trioxide and subsequent alkaline or acidic hydrolysis of the sulfonation products. Other suitable surfactants of the sulfonate type are the alkane sulfonates obtained from C₁₂₋₁₈ alkanes, for example by sulfochlorination or sulfoxidation and subsequent hydrolysis or neutralization. The esters of α -sulfofatty acids (ester sulfonates), for example the α -sulfonated methyl esters of hydrogenated coconut, palm kernel or tallow fatty acids, are also suitable.

Other suitable anionic surfactants are sulfonated fatty acid glycerol esters. Fatty acid glycerol esters in the context of the present invention are the monoesters, diesters and triesters and mixtures thereof which are obtained where production is carried out by esterification of a monoglycerol with 1 to 3 moles of fatty acid or in the transesterification of triglycerides with 0.3 to 2 moles of glycerol. Preferred sulfonated fatty acid glycerol esters are the sulfonation products of saturated fatty acids containing 6 to 22 carbon atoms, for example caproic acid, caprylic acid, capric acid, myristic acid, lauric acid, palmitic acid, stearic acid or behenic acid.

Preferred alk(en)yl sulfates are the alkali metal salts and, in particular, the sodium salts of the sulfuric acid semiesters of C₁₂₋₁₈ fatty alcohols, for example coconut alcohol, tallow alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or C₁₀₋₂₀ oxoalcohols and the corresponding semiesters of secondary alcohols with the same chain length. Other preferred alk(en)yl sulfates are those with the chain length mentioned which contain a synthetic, linear alkyl chain based on a petrochemical and which are

similar in their degradation behavior to the corresponding compounds based on oleochemical raw materials. C₁₂₋₁₆ alkyl sulfates, C₁₂₋₁₅ alkyl sulfates and C₁₄₋₁₅ alkyl sulfates are preferred from the point of view of washing technology. Other suitable anionic surfactants are 2,3-alkyl sulfates which may be produced, for example, in accordance with US 3,234,258 or US 5,075,041 and which are commercially obtainable as products of the Shell Oil Company under the name of DAN®.

The sulfuric acid monoesters of linear or branched C₇₋₂₁ alcohols ethoxylated with 1 to 6 moles of ethylene oxide, such as 2-methyl-branched C₉₋₁₁ alcohols containing on average 3.5 moles of ethylene oxide (EO) or C₁₂₋₁₈ fatty alcohols containing 1 to 4 EO, are also suitable. In view of their high foaming capacity, they are only used in relatively small quantities, for example in quantities of not more than 5% by weight, in dishwashing detergents.

Other suitable anionic surfactants are the salts of alkyl sulfosuccinic acid which are also known as sulfosuccinates or as sulfosuccinic acid esters and which represent monoesters and/or diesters of sulfosuccinic acid with alcohols, preferably fatty alcohols and, more particularly, ethoxylated fatty alcohols. Preferred sulfosuccinates contain C₈₋₁₈ fatty alcohol residues or mixtures thereof. Particularly preferred sulfosuccinates contain a fatty alcohol residue derived from ethoxylated fatty alcohols which, considered in isolation, represent nonionic surfactants (for a description, see below). Of these sulfosuccinates, those of which the fatty alcohol residues are derived from narrow-range ethoxylated fatty alcohols are particularly preferred. Alk(en)yl succinic acid preferably containing 8 to 18 carbon atoms in the alk(en)yl chain or salts thereof may also be used.

Other suitable anionic surfactants are, in particular, soaps. Suitable soaps are saturated fatty acid soaps, such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and

behenic acid, and soap mixtures derived in particular from natural fatty acids, for example coconut oil, palm kernel oil or tallow fatty acids.

The anionic surfactants, including the soaps, may be present in the form of their sodium, potassium or ammonium salts and as soluble salts of organic bases, such as mono-, di- or triethanolamine. The anionic surfactants are preferably present in the form of their sodium or potassium salts and, more preferably, in the form of their sodium salts.

Cleaning tablets according to the invention in the form of laundry detergent or manual dishwashing detergent tablets preferably contain anionic surfactant(s) in quantities of 5 to 50% by weight, preferably in quantities of 7.5 to 40% by weight and more preferably in quantities of 10 to 20% by weight, based on the weight of the tablet.

So far as the choice of the anionic surfactants used in the cleaning tablets according to the invention is concerned, there are no basic requirements to restrict freedom of formulation. Preferred anionic surfactants are the alkyl benzenesulfonates, alkyl sulfates and fatty alcohol sulfates, preferred cleaning tablets in the form of laundry detergent tablets containing 2 to 20% by weight, preferably 2.5 to 15% by weight and more preferably 5 to 10% by weight of fatty alcohol sulfate(s), based on the weight of the tablet.

Nonionic surfactants

Preferred nonionic surfactants are alkoxyated, advantageously ethoxylated, more especially primary alcohols preferably containing 8 to 18 carbon atoms and, on average, 1 to 12 moles of ethylene oxide (EO) per mole of alcohol, in which the alcohol radical may be linear or, preferably, methyl-branched in the 2-position or may contain linear and methyl-branched radicals in the form of the mixtures typically present in oxoalcohol radicals. However, alcohol ethoxylates containing linear radicals of

alcohols of native origin with 12 to 18 carbon atoms, for example coconut oil, palm oil, tallow or oleyl alcohol, and on average 2 to 8 EO per mole of alcohol are particularly preferred. Preferred ethoxylated alcohols include, for example, C₁₂₋₁₄ alcohols containing 3 EO or 4 EO, C₉₋₁₁ alcohol
5 containing 7 EO, C₁₃₋₁₅ alcohols containing 3 EO, 5 EO, 7 EO or 8 EO, C₁₂₋₁₈ alcohols containing 3 EO, 5 EO or 7 EO and mixtures thereof, such as mixtures of C₁₂₋₁₄ alcohol containing 3 EO and C₁₂₋₁₈ alcohol containing 5 EO. The degrees of ethoxylation mentioned represent statistical mean values which, for a special product, can be a whole number or a broken
10 number. Preferred alcohol ethoxylates have a narrow homolog distribution (narrow range ethoxylates, NRE). In addition to these nonionic surfactants, fatty alcohols containing more than 12 EO may also be used, examples including tallow fatty alcohol containing 14 EO, 25 EO, 30 EO or 40 EO.

Another class of preferred nonionic surfactants which may be used
15 either as sole nonionic surfactant or in combination with other nonionic surfactants are alkoxylated, preferably ethoxylated or ethoxylated and propoxylated, fatty acid alkyl esters preferably containing 1 to 4 carbon atoms in the alkyl chain, more especially the fatty acid methyl esters which are described, for example, in Japanese patent application **JP 58/217598**
20 or which are preferably produced by the process described in International patent application **WO-A-90/13533**.

Another class of nonionic surfactants which may advantageously be used are the alkyl polyglycosides (APGs). Suitable alkyl polyglycosides correspond to the general formula RO(G)_z where R is a linear or branched,
25 more particularly 2-methyl-branched, saturated or unsaturated aliphatic radical containing 8 to 22 and preferably 12 to 18 carbon atoms and G stands for a glucose unit containing 5 or 6 carbon atoms, preferably glucose. The degree of glycosidation z is between 1.0 and 4.0, preferably between 1.0 and 2.0 and more preferably between 1.1 and 1.4.

Linear alkyl polyglucosides, i.e. alkyl polyglycosides in which the polyglycosyl moiety is a glucose unit and the alkyl moiety is an n-alkyl group, are preferably used.

The cleaning tablets according to the invention may advantageously contain alkyl polyglycosides, APG contents in the tablets of more than 0.2% by weight, based on the tablet as a whole, being preferred. Particularly preferred cleaning tablets contain APGs in quantities of 0.2 to 10% by weight, preferably in quantities of 0.2 to 5% by weight and more preferably in quantities of 0.5 to 3% by weight.

Nonionic surfactants of the amine oxide type, for example N-cocoalkyl-N,N-dimethylamine oxide and N-tallowalkyl-N,N-dihydroxyethylamine oxide, and the fatty acid alkanolamide type are also suitable. The quantity in which these nonionic surfactants are used is preferably no more than the quantity in which the ethoxylated fatty alcohols are used and, more preferably, no more than half that quantity.

Other suitable surfactants are polyhydroxyfatty acid amides corresponding to formula (I):



in which RCO is an aliphatic acyl group containing 6 to 22 carbon atoms, R¹ is hydrogen, an alkyl or hydroxyalkyl group containing 1 to 4 carbon atoms and [Z] is a linear or branched polyhydroxyalkyl group containing 3 to 10 carbon atoms and 3 to 10 hydroxyl groups. The polyhydroxyfatty acid amides are known substances which may normally be obtained by reductive amination of a reducing sugar with ammonia, an alkylamine or an alkanolamine and subsequent acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

The group of polyhydroxyfatty acid amides also includes compounds

corresponding to formula (II):



in which R is a linear or branched alkyl or alkenyl group containing 7 to 12 carbon atoms, R¹ is a linear, branched or cyclic alkyl group or an aryl group containing 2 to 8 carbon atoms and R² is a linear, branched or cyclic alkyl group or an aryl group or an oxyalkyl group containing 1 to 8 carbon atoms, C₁₋₄ alkyl or phenyl groups being preferred, and [Z] is a linear polyhydroxy-alkyl group, of which the alkyl chain is substituted by at least two hydroxyl groups, or alkoxyated, preferably ethoxyated or propoxyated, derivatives of that group.

[Z] is preferably obtained by reductive amination of a reduced sugar, for example glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy- or N-aryloxy-substituted compounds may then be converted into the required polyhydroxyfatty acid amides by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst, for example in accordance with the teaching of International patent application **WO-A-95/07331**.

According to the invention, preferred cleaning tablets are those containing anionic and nonionic surfactant(s). Performance-related advantages can arise out of certain quantity ratios in which the individual classes of surfactants are used.

For example, particularly preferred cleaning tablets are characterized in that the ratio of anionic surfactant(s) to nonionic surfactant(s) is from 10:1 to 1:10, preferably from 7.5:1 to 1:5 and more preferably from 5:1 to 1:2.

It can be of advantage from the performance point of view if certain classes of surfactants are missing from certain phases of the cleaning

tablets or from the entire tablet, i.e. from every phase. In another important embodiment of the present invention, therefore, at least one phase of the cleaning tablets is free from nonionic surfactants.

Conversely, a positive effect can also be obtained through the presence of certain surfactants in individual phases or in the cleaning tablet as a whole, i.e. in every phase. Introducing the alkyl polyglycosides described above has proved to be of particular advantage, so that cleaning tablets in which at least one phase of the tablet contains alkyl polyglycosides are preferred.

As with the nonionic surfactants, the omission of anionic surfactants from individual phases or from all phases can result in cleaning tablets which are more suitable for certain applications. Accordingly, cleaning tablets where at least one phase of the tablet is free from anionic surfactants are also possible in accordance with the present invention.

15

Builders

Besides deterative ingredients, builders are important ingredients of detergents and cleaners, especially multipurpose cleaners, dishwasher detergents and laundry detergents. The cleaning tablets according to the invention may contain any of the builders typically used in detergents and cleaners, i.e. in particular zeolites, silicates, carbonates/hydrogen carbonates, organic cobuilders and - providing there are no ecological objections to their use - also the phosphates. The builders mentioned may also be used in surfactant-free cleaning tablets so that it is possible in accordance with the invention to produce cleaning tablets which may be used for softening water or as bleach tablets.

20
25

Suitable crystalline layered sodium silicates correspond to the general formula $\text{NaMSi}_x\text{O}_{2x+1y} \cdot \text{H}_2\text{O}$, where M is sodium or hydrogen, x is a number of 1.9 to 4 and y is a number of 0 to 20, preferred values for x

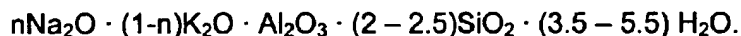
being 2, 3 or 4. Crystalline layered silicates such as these are described, for example, in European patent application **EP-A-0 164 514**. Preferred crystalline layered silicates corresponding to the above formula are those in which M is sodium and x assumes the value 2 or 3. Both β - and δ -sodium
5 disilicates $\text{Na}_2\text{Si}_2\text{O}_5 \cdot y \text{H}_2\text{O}$ are particularly preferred, β -sodium disilicate being obtainable, for example, by the process described in International patent application **WO-A- 91/08171**.

Other useful builders are amorphous sodium silicates with a modulus ($\text{Na}_2\text{O}:\text{SiO}_2$ ratio) of 1:2 to 1:3.3, preferably 1:2 to 1:2.8 and more
10 preferably 1:2 to 1:2.6 which dissolve with delay and exhibit multiple wash cycle properties. The delay in dissolution in relation to conventional amorphous sodium silicates can have been obtained in various ways, for example by surface treatment, compounding, compacting or by overdrying. In the context of the invention, the term "amorphous" is also understood to
15 encompass "X-ray amorphous". In other words, the silicates do not produce any of the sharp X-ray reflexes typical of crystalline substances in X-ray diffraction experiments, but at best one or more maxima of the scattered X-radiation which have a width of several degrees of the diffraction angle. However, particularly good builder properties may even
20 be achieved where the silicate particles produce crooked or even sharp diffraction maxima in electron diffraction experiments. This may be interpreted to mean that the products have microcrystalline regions between 10 and a few hundred nm in size, values of up to at most 50 nm and, more particularly, up to at most 20 nm being preferred. So-called X-
25 ray amorphous silicates such as these, which also dissolve with delay in relation to conventional waterglasses, are described for example in German patent application **DE-A-44 00 024**. Compacted amorphous silicates, compounded amorphous silicates and overdried X-ray-amorphous silicates are particularly preferred.

The finely crystalline, synthetic zeolite containing bound water used in accordance with the invention is preferably zeolite A and/or zeolite P. Zeolite MAP® (Crosfield) is a particularly preferred P-type zeolite. However, zeolite X and mixtures of A, X and/or P are also suitable.

- 5 According to the invention, it is preferred to use, for example, a commercially obtainable co-crystallizate of zeolite X and zeolite A (ca. 80% by weight zeolite X) which is marketed by CONDEA Augusta S.p.A. under the name of VEGOBOND AX® and which may be described by the following formula:

10



- The zeolite may be used both as a builder in a granular compound and for "powdering" the entire mixture to be tabletted, both these options normally
15 being used to incorporate the zeolite in the premix. Suitable zeolites have a mean particle size of less than 10 μm (volume distribution, as measured by the Coulter Counter Method) and contain preferably 18 to 22% by weight and more preferably 20 to 22% by weight of bound water.

- As already mentioned, the generally known phosphates may of
20 course also be used as builders providing their use should not be avoided on ecological grounds. The sodium salts of the orthophosphates, the pyrophosphates and especially the tripolyphosphates, more particularly the pentasodium triphosphate known as sodium tripolyphosphate, are particularly suitable.

- 25 Useful organic builders are, for example, the polycarboxylic acids usable, for example, in the form of their sodium salts, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, benzene hexacarboxylic acid, sugar acids, for example gluconic acid, amino-carboxylic acids, nitrilotriacetic acid (NTA), providing its use is not

ecologically unsafe, and mixtures thereof. Preferred salts are the salts of the polycarboxylic acids, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures thereof.

5 The quantity of builder, particularly in the absence of an effervescent system, is normally between 10 and 70% by weight, preferably between 15 and 60% by weight and more preferably between 20 and 50% by weight. The quantity of builders used is again dependent on the application envisaged so that bleach tablets may contain larger quantities of builders (for example between 20 and 70% by weight, preferably between 25 and 10 65% by weight and more preferably between 30 and 55% by weight) than, for example, laundry detergent tablets (normally 10 to 50% by weight, preferably 12.5 to 45% by weight and more preferably between 17.5 and 37.5% by weight).

15 Since builders, such as the carbonates and hydrogen carbonates and a number of carboxylic acids, can also serve as components of an effervescent system, the quantities mentioned above should not be understood as cumulative in the presence of an effervescent system. If, therefore, the cleaning tablet contains an effervescent system, the quantity of builders additionally present is normally only up to 20% by weight, 20 preferably from 0.01 to 15% by weight, more preferably from 0.1 to 10% by weight and most preferably from 0.3 to 8% by weight, for example 6% by weight, or no additional builder at all is present.

Bleaching agents

25 Among the compounds yielding H_2O_2 in water which serve as bleaching agents, sodium perborate tetrahydrate and sodium perborate monohydrate are particularly important. Other useful bleaching agents are, for example, sodium percarbonate, peroxyphosphates, citrate perhydrates and H_2O_2 -yielding peracidic salts or peracids, such as

perbenzoates, peroxophthalates, diperazelaic acid, phthaloiminoperacid or diperdodecane dioic acid. Where bleaching agents are used, it is again possible to leave out surfactants and/or builders so that pure bleach tablets can be produced. If such bleach tablets are to be used for washing
5 laundry, a combination of sodium percarbonate with sodium sesquicarbonate is preferably used, irrespective of what other ingredients the cleaning tablets contain. If tablets for dishwashing machines are being produced, bleaching agents from the group of organic bleaches may also be used. Typical organic bleaching agents are diacyl peroxides, such as
10 dibenzoyl peroxide for example. Other typical organic bleaching agents are the peroxy acids, of which alkyl peroxy acids and aryl peroxy acids are particularly mentioned as examples. Preferred representatives are (a) peroxybenzoic acid and ring-substituted derivatives thereof, such as alkyl peroxybenzoic acids, but also peroxy- α -naphthoic acid and magnesium
15 monoperphthalate, (b) aliphatic or substituted aliphatic peroxy acids, such as peroxy lauric acid, peroxy stearic acid, ϵ -phthalimidoperoxycaproic acid [phthaloiminoperoxyhexanoic acid (PAP)], o-carboxybenzamidoperoxycaproic acid, N-nonenylamidoperoxadipic acid and N-nonenylamidopersuccinates and (c) aliphatic and araliphatic peroxydicarboxylic acids,
20 such as 1,12-diperoxydicarboxylic acid, 1,9-diperoxyazelaic acid, diperoxysebacic acid, diperoxybrassylic acid, diperoxyphthalic acids, 2-decyldiperoxybutane-1,4-dioic acid, N,N-terephthaloyl-di(6-aminopercaproic acid).

Preferred cleaning tablets according to the invention contain at least one oxygen bleaching agent from the group consisting of alkali metal
25 perborates, alkali metal percarbonates, organic per acids and hydrogen peroxide, more especially from the group consisting of alkali metal perborates and alkali metal percarbonates, more preferably sodium perborate and/or sodium percarbonate.

The cleaning tablets according to the invention contain one or more

bleaching agents in a quantity of normally 0 to 50% by weight, preferably 0.1 to 30% by weight and more preferably 1 to 15% by weight. Bleach tablets, such as stain remover tablet, naturally contain large amounts of bleaching agents whereas laundry, dishwasher detergent tablets contain
5 medium amounts of bleaching agent and cleaning tablets, such as lavatory cleaner tablets, generally contain only small amounts of bleaching agent of up to 5% by weight, for example 1 or 2% by weight, or no bleaching agent at all.

Other suitable bleaching agents, particularly in dishwasher tablets
10 and cleaner tablets, are chlorine- or bromine-releasing substances. Suitable chlorine- or bromine-releasing materials are, for example, heterocyclic N-bromamides and N-chloramides, for example trichloroisocyanuric acid, tribromoisocyanuric acid, dibromoisocyanuric acid and/or dichloroisocyanuric acid (DICA) and/or salts thereof with cations,
15 such as potassium and sodium. Hydantoin compounds, such as 1,3-dichloro-5,5-dimethyl hydantoin, are also suitable as are hypochlorites and other typical chlorine-containing bleaching agents.

In order to obtain an improved bleaching effect where cleaning or washing is carried out at temperatures of 60°C or lower, bleach activators
20 may be incorporated. The bleach activators may be compounds which form aliphatic peroxocarboxylic acids containing preferably 1 to 10 carbon atoms and more preferably 2 to 4 carbon atoms and/or optionally substituted perbenzoic acid under perhydrolysis conditions. Substances bearing O- and/or N-acyl groups with the number of carbon atoms
25 mentioned and/or optionally substituted benzoyl groups are suitable. Preferred bleach activators are polyacylated alkylenediamines, more particularly tetraacetyl ethylenediamine (TAED), acylated triazine derivatives, more particularly 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, more particularly tetraacetyl glycoluril

(TAGU), N-acylimides, more particularly N-nonanoyl succinimide (NOSI), acylated phenol sulfonates, more particularly n-nonanoyl or isononanoyloxybenzenesulfonate (n- or iso-NOBS), carboxylic anhydrides, more particularly phthalic anhydride, acylated polyhydric alcohols, more particularly triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran.

In addition to or instead of the conventional bleach activators mentioned above, so-called bleach catalysts may also be incorporated in the cleaning tablets. Bleach catalysts are bleach-boosting transition metal salts or transition metal complexes such as, for example, manganese-, iron-, cobalt-, ruthenium- or molybdenum-salen complexes or carbonyl complexes. Manganese, iron, cobalt, ruthenium, molybdenum, titanium, vanadium and copper complexes with nitrogen-containing tripod ligands and cobalt-, iron-, copper- and ruthenium-amine complexes may also be used as bleach catalysts.

The bleaching performance of bleach-containing cleaning tablets, such as laundry detergent tablets, cleaner tablets or bleach tablets, is preferably increased by the use of bleach activators. Thus, in one particular embodiment, cleaning tablets according to the invention contain at least one bleach activator, preferably from the group of polyacylated alkylenediamines, more particularly tetraacetyl ethylenediamine (TAED), N-acyl imides, more particularly N-nonanoyl succinimide (NOSI), acylated phenol sulfonates, more particularly n-nonanoyl or isononanoyloxybenzenesulfonate (n- or iso-NOBS), n-methyl morpholinium acetonitrile methyl sulfate (MMA) and/or bleach-boosting transition metal complexes, more particularly containing the central atoms Mn, Fe, Co, Cu, Mo, V, Ti and/or Ru, preferably selected from the group of manganese and/or cobalt salts and/or complexes, more preferably the cobalt (amine) complexes, cobalt (acetate) complexes, cobalt (carbonyl) complexes,

chlorides of cobalt or manganese and manganese sulfate.

The cleaning tablets according to the invention may contain, for example between 0.5 and 30% by weight, preferably between 1 and 20% by weight and more preferably between 2 and 15% by weight, based on the tablet as a whole, of one or more bleach activators or bleach catalysts. These quantities may vary according to the application envisaged for the cleaning tablets. Thus, in typical heavy-duty detergent tablets, bleach activator contents of 0.5 to 10% by weight, preferably between 2 and 8% by weight and more preferably between 0.5 and 10% by weight are normal whereas bleach tablets contain much larger amounts, for example between 5 and 30% by weight, preferably between 7.5 and 25% by weight and more preferably between 10 and 20% by weight. The expert is not restricted in his freedom of formulation and can thus produce laundry detergent tablets, cleaner tablets or bleach tablets with a relatively strong or weak bleaching effect by varying the contents of bleach activator and bleaching agent.

A particularly preferred bleach activator is N,N,N',N'-tetraacetyl ethylenediamine which is widely used in detergents. Accordingly, preferred cleaning tablets are characterized in that tetraacetyl ethylenediamine in the quantities mentioned above is used as bleach activator.

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Corrosion inhibitors

To protect the tableware or the machine itself, dishwashing tablets according to the invention may contain corrosion inhibitors, silver protectors being particularly important for dishwashing machines. Above all, silver protectors selected from the group of triazoles, benzotriazoles, bisbenzotriazoles, aminotriazoles, alkylaminotriazoles and the transition metal salts or complexes may generally be used. Benzotriazole and/or alkylaminotriazole is/are particularly preferred. In addition, dishwashing formulations often contain corrosion inhibitors containing active chlorine

which are capable of distinctly reducing the corrosion of silver surfaces. Chlorine-free dishwashing detergents contain in particular oxygen- and nitrogen-containing organic redox-active compounds, such as dihydric and trihydric phenols, for example hydroquinone, pyrocatechol, hydroxy-
5 hydroquinone, gallic acid, phloroglucinol, pyrogallol and derivatives of these compounds. Salt-like and complex-like inorganic compounds, such as salts of the metals Mn, Ti, Zr, Hf, V, Co and Ce are also frequently used. Of these, the transition metal salts selected from the group of manganese and/or cobalt salts and/or complexes are preferred, cobalt(amine)
10 complexes, cobalt(acetate) complexes, cobalt(carbonyl) complexes, chlorides of cobalt or manganese and manganese sulfate being particularly preferred. Zinc compounds may also be used to prevent corrosion of tableware.

15 Soil-release compounds

Particular ingredients which may be used in cleaning tablets according to the invention for machine dishwashing or for the cleaning of hard surfaces are substances which prevent the resoiling of surfaces and/or facilitate the release of soil after a single application (so-called soil-
20 release compounds).

Suitable soil-release compounds are any of the compounds known from the prior art. Particularly suitable soil-release compounds are cationic polymers such as, for example, hydroxypropyl trimethyl ammonium guar; copolymers of aminoethyl methacrylate and acrylamide and copolymers of
25 dimethyl diallyl ammonium chlorider and acrylamide, polymers containing imino groups, cationic cellulose derivatives, cationic homo- and/or copolymers (monomer units: quaternized ammonium alkyl methacrylate groups).

Particularly preferred soil-release compounds are the cationic

polymers selected from cationic polymers of copolymers of such monomers as trialkyl ammonium alkyl (meth)acrylate or acrylamide; dialkyl diallyl diammonium salts; polymer-analog reaction products of ethers or esters of polysaccharides with lateral ammonium groups, more particularly guar, cellulose and starch derivatives; polyadducts of ethylene oxide with ammonium groups; quaternary ethylene imine polymers and polyesters and polyamides containing quaternary lateral groups as soil-release compounds. Natural polyuronic acids and related substances and also polyampholytes and hydrophobicized polyampholytes and mixtures of these substances are also particularly preferred for the purposes of the present invention.

Enzymes

Suitable enzymes are those from the class of proteases, lipases, amylases, cellulases or mixtures thereof. Enzymes obtained from bacterial strains or fungi, such as *Bacillus subtilis*, *Bacillus licheniformis* and *Streptomyces griseus*, are particularly suitable. Proteases of the subtilisin type are preferred, proteases obtained from *Bacillus lentus* being particularly preferred. Enzyme mixtures, for example of protease and amylase or protease and lipase or protease and cellulase or of cellulase and lipase or of protease, amylase and lipase or of protease, lipase and cellulase, but especially cellulase-containing mixtures, are of particular interest. Peroxidases or oxidases have also proved to be suitable in some cases. The enzymes may be adsorbed to supports and/or encapsulated in membrane materials to protect them against premature decomposition. The percentage content of the enzymes, enzyme mixtures or enzyme granules in the cleaning tablets according to the invention, more particularly in laundry and dishwashing detergent tablets may be, for example, from about 0.1 to 5% by weight and is preferably from 0.1 to about 2% by weight.

The most commonly used enzymes include lipases, amylases, cellulases and proteases. Preferred proteases are, for example, BLAP® 140 (Biozym), Optimase® M-440 and Opticlean® M-250 (Solvay Enzymes); Maxacal® CX and Maxapem® or Esperase® (Gist Brocades) and even Savinase® (Novo). Particularly suitable cellulases and lipases are Celluzym® 0,7 T and Lipolase® 30 T (Novo Nordisk). Particularly suitable amylases are Duramyl® and Termamyl® 60 T and Termamyl® 90 T (Novo), Amylase-LT® (Solvay Enzymes) and Maxamyl® P5000 (Gist Brocades). Other enzymes may also be used.

10

Soil repellents

In addition, the cleaning tablets according to the invention, more particularly laundry detergent and stain remover tablets, may also contain components with a positive effect on the removal of oil and fats from textiles by washing (so-called soil repellents). This effect becomes particularly clear when a textile which has already been repeatedly washed with a detergent according to the invention containing this oil- and fat-dissolving component is soiled. Preferred oil- and fat-dissolving components include, for example, nonionic cellulose ethers, such as methyl cellulose and methyl hydroxypropyl cellulose containing 15 to 30% by weight of methoxyl groups and 1 to 15% by weight of hydroxypropoxyl groups, based on the nonionic cellulose ether, and the polymers of phthalic acid and/or terephthalic acid known from the prior art or derivatives thereof, more particularly polymers of ethylene terephthalates and/or polyethylene glycol terephthalates or anionically and/or nonionically modified derivatives thereof. Of these, the sulfonated derivatives of phthalic acid and terephthalic acid polymers are particularly preferred.

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Optical brighteners

The cleaning tablets, more particularly laundry detergent tablets, may contain derivatives of diaminostilbenedisulfonic acid or alkali metal salts thereof as optical brighteners. Suitable optical brighteners are, for example, salts of 4,4'-bis-(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino)-stilbene-2,2'-disulfonic acid or compounds of similar composition which contain a diethanolamino group, a methylamino group, an anilino group or a 2-methoxyethylamino group instead of the morpholino group. Brighteners of the substituted diphenyl styryl type, for example alkali metal salts of 4,4'-bis-(2-sulfostryl)-diphenyl, 4,4'-bis-(4-chloro-3-sulfostryl)-diphenyl or 4-(4-chlorostyryl)-4'-(2-sulfostryl)-diphenyl, may also be present. Mixtures of the brighteners mentioned above may also be used.

The optical brighteners are used in the cleaning tablets according to the invention, more particularly laundry detergent tablets, in concentrations of 0.01 to 1% by weight, preferably in concentrations of 0.05 to 0.5% by weight and more preferably in concentrations of 0.1 to 0.25% by weight, based on the tablet as a whole.

Dyes and perfumes

Dyes and perfumes are added to the cleaning tablets according to the invention to improve the aesthetic impression created by the products and to provide the consumer not only with the required washing performance but also with a visually and sensorially "typical and unmistakable" product. Suitable perfume oils or fragrances include individual perfume compounds, for example synthetic products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon type. Perfume compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert.butyl cyclohexyl acetate, linalyl acetate, dimethyl benzyl carbonyl acetate, phenyl ethyl acetate, linalyl benzoate,

benzyl formate, ethyl methyl phenyl glycinate, allyl cyclohexyl propionate, styrallyl propionate and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals containing 8 to 18 carbon atoms, citral, citronellal, citronellyloxy-
5 acetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilial and bourgeonal; the ketones include, for example, the ionones, α -isomethyl ionone and methyl cedryl ketone; the alcohols include anethol, citronellol, eugenol, geraniol, linalool, phenyl ethyl alcohol and terpineol and the hydrocarbons include, above all, the terpenes, such as limonene and pinene. However,
10 mixtures of various perfumes which together produce an attractive perfume note are preferably used. Perfume oils such as these may also contain natural perfume mixtures obtainable from vegetable sources, for example pine, citrus, jasmine, patchouli, rose or ylang-ylang oil. Also suitable are clary oil, camomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, lime
15 blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil and labdanum oil and orange blossom oil, neroli oil, orange peel oil and sandalwood oil.

The dye content is normally below 0.1% by weight and, more particularly, below 0.05% by weight while perfumes may make up as much
20 as 2% by weight and more particularly from 0.1 to 0.5% by weight of the formulation as a whole.

The perfumes may be directly incorporated in the tablets, although it can also be of advantage to apply the perfumes to supports which strengthen the adherence of the perfume to the washing and which provide
25 the textiles with a long-lasting fragrance through a slower release of the perfume. Suitable support materials are, for example, cyclodextrins, the cyclodextrin/perfume complexes optionally being coated with other auxiliaries.

In order to improve their aesthetic impression, the cleaning tablets

according to the invention may be colored with suitable dyes. Preferred dyes, which are not difficult for the expert to choose, have high stability in storage, are not affected by the other ingredients of the tablets or by light and do not have any pronounced substantivity for the treated substrates, for example textile fibers or tableware, so as not to color them.

Any dyes which can be destroyed by oxidation in the washing process and mixtures thereof with suitable blue dyes, so-called blueing agents, are preferably used in the cleaning tablets according to the invention. It has proved to be of advantage to use dyes which are soluble in water or - at room temperature - in liquid organic substances. Suitable dyes are, for example, anionic dyes, for example anionic nitroso dyes. One possible dye is, for example, naphthol green (Color Index (CI) Part 1: Acid Green 1; Part 2: 10020), which is commercially available for example as Basacid® Grün 970 from BASF, Ludwigshafen, and mixtures thereof with suitable blue dyes. Other suitable dyes are Pigmosol® Blau 6900 (CI 74160), Pigmosol® Grün 8730 (CI 74260), Basonyl® Rot 545 FL (CI 45170), Sandolan® Rhodamin EB 400 (CI 45100), Basacid® Gelb 094 (CI 47005), Sicovit® Patentblau 85 E 131 (CI 42051), Acid Blue 183 (CAS 12217-22-0, CI Acid Blue 183), Pigment Blue 15 (CI 74160), Supranol® Blau GLW (CAS 12219-32-8, CI Acid Blue 221), Nylosan® Gelb N-7GL SGR (CAS 61814-57-1, CI Acid Yellow 218) and/or Sandolan® Blau (CI Acid Blue 182, CAS 12219-26-0).

In selecting the dye for cleaning tablets for the treatment of textile surfaces, more particularly for laundry detergent and stain remover tablets, it is important to ensure that the dye does not have an excessive affinity for the textile surfaces and, in particular, for synthetic fibers. Another factor to be taken into account in the selection of suitable dyes is that dyes differ in their stability to oxidation. Generally speaking, water-insoluble dyes are more stable to oxidation than water-soluble dyes. The concentration of the

dye in the detergents varies according to its solubility and hence its sensitivity to oxidation. In the case of readily water-soluble dyes, for example the above-mentioned Basacid® Grün and Sandolan® Blau, dye concentrations in the range from a few 10^{-2} to 10^{-3} % by weight are typically selected. By contrast, in the case of the pigment dyes which are particularly preferred for their brilliance, but which are less readily soluble in water, for example the above-mentioned Pigmosol® dyes, suitable concentrations of the dye in cleaners or laundry detergents are typically of the order of a few 10^{-3} to 10^{-4} % by weight.

10

Antimicrobial agents

In order to provide the cleaning tablets according to the invention with antimicrobial activity or merely to preserve them, one or more antimicrobial agents may be present, preferably being selected from the groups of alcohols, aldehydes, antimicrobial acids, carboxylic acid esters, acid amides, phenols, phenol derivatives, diphenyls, diphenyl alkanes, urea derivatives, oxygen acetals and formals, nitrogen acetals and formals, benzamidines, substituted isothiazoles and hydrogenated isothiazole derivatives, such as isothiazolines (dihydroisothiazoles) and isothiazolidines, phthalimide derivatives, pyridine derivatives, antimicrobial surface-active compounds, such as antimicrobial quaternary surface-active compounds, guanidines, antimicrobial amphoteric compounds, quinolines, 1,2-dibromo-2,4-dicyanobutane, iodo-2-propynyl butyl carbamate, iodine, iodophores and peroxides, for example phenoxyethanol, undecylenic acid, salicylic acid, benzoic acid, , 2-benzyl-4-chlorophenol, 2,2'-methylene-bis-(6-bromo-4-chlorophenol), 2,4,4'-trichloro-2'-hydroxydiphenyl ether, N-(4-chlorophenyl)-N-(3,4-dichlorophenyl)-urea, N,N'-(1,10-decanediyl-di-1-pyridinyl-4-ylidene)-bis-(1-octanamine)-dihydrochloride and N,N'-bis-(4-chlorophenyl)-3,12-diimino-2,4,11,13-tetraazatetradecane diimidoamide, as

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described, for example in *K.H. Wallhäußer "Praxis der Sterilisation, Desinfektion - Konservierung : Keimidentifizierung - Betriebshygiene"* (5th Edition, Stuttgart/New York: Thieme, 1995).

5 The cleaning tablets according to the invention preferably contain salicylic acid and/or isothiazolines as their antimicrobial component.

The content of one or more antimicrobial agents is normally between 0 and 10% by weight, preferably between 0.001 and 5% by weight, more preferably between 0.01 and 2% by weight, most preferably between 0.05 and 1% by weight and, in one most particularly preferred embodiment,
10 between 0.1 and 0.5% by weight.

Fillers

Fillers (extenders, INCI Bulking Agents) are - generally relatively inexpensive - often chemically inert solids which are added to increase
15 volume and/or weight or to dilute the other solids and, in many cases, also to improve usability. Fillers are also used to adjust the form in which a product is to be marketed and/or its concentration.

Suitable fillers are carbonates, more particularly calcium carbonate, and also silicates (talcum, clay, mica), silica, calcium and barium sulfate,
20 aluminium hydroxide and cellulose powders or microcrystalline cellulose and lactose, sucrose, mannitol and sorbitol and also starch and dicalcium phosphate.

A particularly preferred filler is sodium sulfate. Fillers, such as sodium sulfate, also act as an auxiliary for improving processability in
25 production and flow behavior, for preventing lump formation and dust emission, as a carrier and for correcting powder properties.

Other suitable fillers are, for example, the following fillers referred to by their INCI names which are described in more detail in *International Cosmetic Ingredient Dictionary and Handbook*: Alumina, Aluminum Silicate,

Amylodextrin, Attapulgit, Barley (*Hordeum Distichon*) Flour, Barley
 (*Hordeum Vulgare*) Flour, Bentonite, Betaglucan, Biotite, Calcium
 Aluminum Borosilicate, Calcium Carbonate, Calcium Caseinate, Calcium
 Phosphate, Calcium Silicate, Calcium Sodium Borosilicate, Calcium
 5 Sulfate, Cellulose, Chalk, Chitin, Coconut (*Cocos Nucifera*) Shell Powder,
 Colloidal Oatmeal, Corn (*Zea Mays*) Cob Meal, Corn (*Zea Mays*) Flour,
 Corn (*Zea Mays*) Gluten Protein, Corn (*Zea Mays*) Meal, Croscarmellose,
 Dextran, Dextrin, Diatomaceous Earth, Fuller's Earth, Hectorite, Hydrated
 Silica, Hydroxyapatite, Hydroxypropyl Starch Phosphate, Isomalt, Kaolin,
 10 Lithium Magnesium Silicate, Lithium Magnesium Sodium Silicate, Loess,
 Magnesium Carbonate, Magnesium Carbonate Hydroxide, Magnesium
 Silicate, Magnesium Stearate, Magnesium Sulfate, Magnesium Tallowate,
 Magnesium Trisilicate, Microcrystalline Cellulose, Microcrystalline Wax,
 Montmorillonite, Moroccan Lava Clay, Nylon-6, Nylon-11, Nylon-12, Nylon-
 15 66, Oat (*Avena Sativa*) Bran, Oat (*Avena Sativa*) Flour, Oat (*Avena Sativa*)
 Meal, Peach (*Prunus Persica*) Pit Powder, Peanut (*Arachis Hypogaea*)
 Flour, Pecan (*Carya Illinoensis*) Shell Powder, Perlite, Polydextrose,
 Polyethylene, Polyoxymethylene Melamine Urea, Polyoxymethylene Urea,
 Polypropylene, Potato (*Solanum Tuberosum*) Starch, PTFE, Pumice,
 20 Rayon, Rice (*Oryza Sativa*) Bran, Rice (*Oryza Sativa*) Starch, Rye (*Secale*
Cereale) Flour, Silica, Silica Dimethyl Silylate, Silica Silylate, Silk, Silk
 Powder, Sodium Hydroxypropyl Starch Phosphate, Sodium Magnesium
 Silicate, Soybean Flour (*Glycine Soja*), Sweet Almond (*Prunus Amygdalus*
Dulcis) Meal, Talc, Tin Oxide, Titanium Hydroxide, Trimagnesium
 25 Phosphate, Walnut (*Juglans Mandshurica*) Shell Powder, Walnut (*Juglans*
Regia) Shell Powder, Wheat (*Triticum Vulgare*) Bran, Wheat (*Triticum*
Vulgare) Flour, Wheat (*Triticum Vulgare*) Powder, Wheat (*Triticum Vulgare*)
 Starch, Wood Powder, Zinc Borosilicate and Zinc Oxide.

Binders

Binders (dry binders, INCI Binders) impart adhesive properties during and after the tableting of a particulate premix to form cleaning tablets according to the invention. Many liquids, surfactants and polymers
 5 may be used as binders. In selecting the binder, it is important to ensure that the effect of the disintegration aid is not adversely influenced.

Suitable binders are, for example, lactose, sucrose, mannitol, sorbitol, microcrystalline cellulose, starch, dicalcium phosphate, starch, alginates, polyvinyl pyrrolidone (PVP) and carboxymethyl cellulose.
 10 Binders particularly suitable for granulation are starch, alginates, polyvinyl pyrrolidone and, more particularly, carboxymethyl cellulose.

A particularly preferred binder is polyvinyl pyrrolidone (PVP).

Other suitable binders are, for example, the following binders referred to by their INCI names which are described in more detail in
 15 *International Cosmetic Ingredient Dictionary and Handbook*:
 Acrylamide/Ammonium Acrylate Copolymer, Acrylamide/Sodium Acrylate Copolymer, Acrylates/Acrylamide Copolymer, Acrylates/Ammonium Methacrylate Copolymer, Acrylates Copolymer, Acrylates/Dimethicone Copolymer, Acrylates/Dimethylaminoethyl Methacrylate Copolymer,
 20 Acrylates/PVP Copolymer, Acrylates/VA Copolymer, Acrylic Acid/Acrylonitrogens Copolymer, Agar, Algin, Alginic Acid, Ammonium Acrylates/Acrylonitrogens Copolymer, Ammonium Acrylates Copolymer, Ammonium Alginate, Ammonium VA/Acrylates Copolymer, Amylopectin, Beeswax, Behenyl Alcohol, Butylated PVP, Butyl Ester of Ethylene/MA
 25 Copolymer, Butyl Ester of PVM/MA Copolymer, Calcium Caseinate, C1-5 Alkyl Galactomannan, Carboxymethyl Hydroxyethylcellulose, Carboxymethyl Hydroxypropyl Guar, Cellulose Acetate Propionate Carboxylate, Cellulose Gum, Ceresin, Collodion, Corn (Zea Mays) Flour, Croscarmellose, Dextran, Dextran Sulfate, Dextrin, Dibutylhexyl IPDI,

Didecyltetradecyl IPDI, Diglycereth-7 Malate, Dilinoleic
 Acid/Ethylenediamine Copolymer, Dioctyldecyl IPDI, Dioctyldodecyl IPDI,
 Dioctyl IPDI, Distarch Glyceryl Ether, Distarch Phosphate, Ethylcellulose,
 Ethylene/Acrylic Acid Copolymer, Ethylene/Acrylic Acid/VA Copolymer,
 5 Ethylene/Calcium Acrylate Copolymer, Ethylene/MA Copolymer,
 Ethylene/Magnesium Acrylate Copolymer, Ethylene/Sodium Acrylate
 Copolymer, Ethylene/VA Copolymer, Ethyl Ester of PVM/MA Copolymer,
 Gelatin, Glyceryl Starch, Guar (Cyanopsis Tetragonoloba) Gum,
 Hydroabietyl Alcohol, Hydrogenated Japan Wax, Hydrogenated Jojoba
 10 Wax, Hydrogenated Microcrystalline Wax, Hydrogenated Rice Bran Wax,
 Hydrogenated Rosin, Hydroxybutyl Methylcellulose, Hydroxyethylcellulose,
 Hydroxyethyl Ethylcellulose, Hydroxylated Lanolin, Hydroxypropylcellulose,
 Hydroxypropyl Guar, Hydroxypropyl Methylcellulose, Isopropyl Ester of
 PVM/MA Copolymer, Isopropylidenediphenol Bishydroxypropyl PEG-180,
 15 Isopropyl Isostearate, Isopropyl Lanolate, Isopropyl Laurate, Isopropyl
 Linoleate, Isopropyl Myristate, Isopropyl Oleate, Isopropyl Palmitate,
 Isopropyl Stearate, Isopropyl Tallowate, Isostearic Acid, Isostearyl
 Isostearate, Isostearyl Myristate, Isostearyl Neopentanoate, Isostearyl
 Palmitate, Japan (Rhus Succedanea) Wax, Karaya (Sterculia Urens) Gum,
 20 Lanolin Alcohol, Lanolin Wax, Lithium Magnesium Silicate, Lithium
 Stearate, Locust Bean (Ceratonia Siliqua) Gum, Maltodextrin, Mannitol,
 Methoxypolyoxymethylene Melamine, Methylcellulose, Methyl
 Ethylcellulose, Microcrystalline Wax, Montan Acid Wax, Montan Wax,
 Oleostearine, Ouricury Wax, Ozokerite, Pectin, PEG-5M, PEG-7M, PEG-
 25 9M, PEG-14M, PEG-20M, PEG-23M, PEG-25M, PEG-45M, PEG-90M,
 PEG-115M, PEG-160M, PEG-100/IPDI Copolymer, Pentaerythrityl
 Tetraabietate, Pentaerythrityl Tetrabehenate, Pentaerythrityl
 Tetrabenzoate, Pentaerythrityl Tetracocoate, Pentaerythrityl
 Tetraisostearate, Pentaerythrityl Tetralaurate, Pentaerythrityl

Tetraoctanoate, Pentaerythrityl Tetraoleate, Pentaerythrityl
 Tetrapelargonate, Pentaerythrityl Tetrastearate, Pentaerythrityl Trioleate,
 Piperylene/Butene/Pentene Copolymer, Polyacrylamide, Polyacrylic Acid,
 Polybutene, Polybutyl Acrylate, Polydipentene, Polyethylacrylate,
 5 Polyethylene, Polyisobutene, Polyurethane-1, Polyvinyl Acetate, Polyvinyl
 Alcohol, Polyvinyl Butyral, Polyvinyl Laurate, Polyvinyl Methyl Ether,
 Potassium Alginate, Potassium Aluminum Polyacrylate, Potassium
 Carrageenan, Potato (*Solanum Tuberosum*) Starch, PPG-6-Sorbeth-245,
 PPG-6-Sorbeth-500, Propylene Glycol Alginate, PVM/MA Copolymer, PVP,
 10 PVP/Decene Copolymer, PVP/Dimethylaminoethylmethacrylate
 Copolymer, PVP/Eicosene Copolymer, PVP/Hexadecene Copolymer,
 PVP/VA Copolymer, PVP/VA/Itaconic Acid Copolymer, Rosin, Shellac,
 Shellac Wax, Sodium Acrylate/Vinyl Alcohol Copolymer, Sodium Acrylates
 Copolymer, Sodium Acrylates/Acrolein Copolymer, Sodium
 15 Acrylates/Acrylonitrogens Copolymer, Sodium Carboxymethyl Betaglukan,
 Sodium Carboxymethyl Dextran, Sodium Carboxymethyl Starch, Sodium
 Carrageenan, Sodium Cellulose Sulfate, Sodium C4-12 Olefin/Maleic Acid
 Copolymer, Sodium Magnesium Silicate, Sodium Polyacrylate Starch,
 Sodium Polymethacrylate, Styrene/MA Copolymer, Synthetic Beeswax,
 20 Synthetic Candelilla Wax, Synthetic Carnauba, Synthetic Japan Wax,
 Synthetic Wax, Tragacanth (*Astragalus Gummifer*) Gum,
 Triethoxycaprylylsilane, Trimethoxycaprylylsilane, VA/Crotonates
 Copolymer, Wheat (*Triticum Vulgare*) Gluten, Wheat (*Triticum Vulgare*)
 Starch and Xanthan Gum.

25

Dust binding agents

Particular binding agents are dust binding agents which are used to
 prevent dust emission during and after tableting of the particulate premix to
 form cleaning tablets according to the invention.

Preferred dust binding agents are silicone oils and, more particularly, paraffin oils. One or more dust binding agents, more particularly one or more paraffin oils, are used in quantities of normally not more than 3% by weight, preferably from 0.02 to 1% by weight and more preferably from 0.1 to 1% by weight.

Release agents

Silicon dioxide

Release agents are solid or liquid substances which reduce the adhesion forces between two adjoining surfaces (for example molding/mold), i.e. prevent them from sticking by forming a readily removable film between the two surfaces (abhesive agent). General properties of release agents are chemical inertness, favorable spreading behavior and a melting point adapted to the particular processing method. Release agents are used in the form of dispersions (emulsions or suspensions), sprays, pastes, powders and permanent, generally baked-on films. The films can be produced by spraying on, spread coating or immersion of the mold. An exception are the so-called internal release agents which are mixed into the material to be demolded and which are either capable of accumulating on the surface of the molding or promote fairly rapid curing of the surface so that no bond is established between the wall of the mold and the molding.

The most important classes of release agents are silicones in the form of oils, oil emulsions in water, fats and resins, waxes (largely natural and synthetic paraffins with and without functional groups), metal soaps (metal salts of fatty acids, such as calcium, lead, magnesium, aluminium, zinc stearate), fats, polymers (polyvinyl alcohol, polyesters and polyolefins), fluorocarbons, inorganic release agents in the form of powders (such as silicon dioxide, graphite, talcum and mica).

Preferred release agents are the metal soaps and paraffin oils.

Release agents are used as mold release agents in the pharmaceutical industry in the production of tablets and dragées (where the stearates and talcum used also act as lubricants).

Release agents are also known by such special names as adhesive
5 agents, lubricants and flow aids.

Lubricants

Lubricants are additives for filled plastic compounds (molding compounds) which are used to make the fillers slide more easily and,
10 hence, the molding compounds easier to mold. Metal soaps and siloxane combinations are suitable for this purpose. Known lubricants are metal soaps, wax and paraffin dispersions, sulfated oils and PE waxes, silicone oils, paraffin oils.

Suitable lubricants are, for example, starch, talcum and silicon
15 dioxide.

Flow aids

Flow aids are any auxiliaries which are added to powder-form or granulated, more particularly hygroscopic, substances in small quantities to
20 prevent them from forming lumps or agglomerating and thus permanently to guarantee free flow. They are sometimes referred to as fluidifiers. Suitable flow aids, which are also known as adhesives, anticaking agents and fluidifiers, are water-insoluble hydrophobicizing or moisture-adsorbing powders of kieselghur, pyrogenic silicas, tricalcium phosphate, calcium
25 silicates, Al_2O_3 , MgO , MgCO_3 , ZnO , stearates, fatty amines and the like.

Metal soaps

Metal soaps are the salts of the metals Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Ni, Pb, Sn, Sr, Zn (not Na or K) with higher fatty, resinic and

naphthenic acids (stearates, palmitates, oleates, linoleates, resinates, laurates, octanoates, ricinoleates, 12-hydroxystearates, naphthenates, tallates and the like). The metal soaps melt between 15 and 200°C and generally show colloidal behavior and interfacial activity. Their solubility in water is poor. In general, they swell on initial contact with water. In addition, metal soaps, more particularly Ca, Li, Sr, Ba, Pb, Mn and Mg soaps, act as lubricants in the production of cleaning tablets.

A particularly preferred metal soap is magnesium stearate.

The cleaning tablets according to the invention contain one or more metal soaps, more particularly magnesium stearate, in a quantity of normally 0 to 10% by weight, preferably 0.1 to 5% by weight and more preferably 1 to 3% by weight.

Powdering materials

Before the particulate premix is compressed to form cleaning tablets, it may be "powdered" with fine-particle surface treatment materials. This can be of advantage to the quality and physical properties of both the premix (storage, tableting) and the final cleaning tablets. Fine-particle powdering materials have been known for some time in the art, zeolites, silicates and other inorganic salts generally being used. However, the compound is preferably "powdered" with fine-particle zeolite, zeolites of the faujasite type being preferred. In the context of the present invention, the expression "zeolite of the faujasite type" encompasses all three zeolites which form the faujasite subgroup of zeolite structural group 4 (cf. Donald W. Breck: **"Zeolite Molecular Sieves"** John Wiley & Sons, New York/London/Sydney/Toronto, 1974, page 92). Besides zeolite X, therefore, zeolite Y and faujasite and mixtures of these compounds may also be used, pure zeolite X being preferred.

Mixtures or co-crystallizates of faujasite zeolites with other zeolites

which do not have to belong to zeolite structural group 4 may also be used as powdering materials, in which case at least 50% by weight of the powdering material consists of a faujasite zeolite.

5 Production

The cleaning tablets according to the invention are produced by first dry mixing the constituents of the individual phases, which may be completely or partly pregranulated, and then forming/shaping, more particularly tableting, the resulting mixtures using conventional processes. To produce the cleaning tablets according to the invention, the premix is compacted between two punches in a die to form a solid compactate. This process, which is referred to in short hereinafter as tableting, comprises four phases, namely metering, compacting (elastic deformation), plastic deformation and ejection.

15 In the most simple case where the cleaning tablets are produced by the application of pressure to a premix to be tableted which is accommodated in the cavity of a press – hereinafter referred to simply as tableting – the mixture to be tableted is compressed directly, i.e. without preliminary granulation. The advantages of this so-called direct tableting are its simple and inexpensive application because no other process steps
20 and hence no other items of equipment are involved. However, these advantages are offset by disadvantages. Thus, a powder mixture which is to be directly tableted must possess adequate plastic deformability and good flow properties and must not show any tendency to separate during
25 storage, transportation and filling of the die. If a powder mixture satisfies these three requirements, the tablets are preferably produced by direct tableting. By contrast, if these three requirements are not satisfied by a particular mixture or are difficult to satisfy, direct tableting is preferably not used for the production of tablets according to the invention, instead

powder-form components ("primary particles") are agglomerated or granulated by suitable methods to secondary particles with larger particle diameters. These granules or mixtures of different granules are then mixed with individual powder-form additives and the resulting mixtures are
5 tabletted. In one particular embodiment of the invention, preferred cleaning tablets are obtained by tableting a particulate premix of at least one batch of surfactant-containing granules and at least one subsequently added powder-form component. The surfactant-containing granules may be produced by conventional granulation processes, such as mixer and pan
10 granulation, fluidized bed granulation, extrusion, pelleting or compacting. It is of advantage so far as the subsequent detergent tablets are concerned if the premix to be tabletted has a bulk density of at least 500 g/l, preferably of at least 600 g/l and more preferably above 700 g/l. Another advantage can arise out of a relatively narrow particle size distribution of the surfactant
15 granules used. According to the invention, preferred cleaning tablets are those in which the granules have particle sizes of 10 to 4,000 μm , preferably between 100 and 2,000 μm and more preferably between 600 and 1,400 μm . According to the invention, preferred cleaning tablets consist of a particulate premix containing granular components and
20 subsequently incorporated powder-form components, the, or one of the, fine-particle components subsequently incorporated being a zeolite of the faujasite type with particle sizes below 100 μm , preferably below 10 μm and more preferably below 5 μm and making up at least 0.2% by weight, preferably at least 0.5% by weight and more preferably more than 1% by
25 weight of the premix to be compressed. The fine-particle aftertreatment components with the particle sizes mentioned above may be dry-mixed with the premix to be tabletted. However, it is also possible and preferred to "stick" them onto the surface of the relatively coarse particles by addition of small quantities of liquid components. These powdering techniques are

widely described in the prior art literature and familiar to the expert. Liquid components suitable as adhesion promoters for the powdering materials are, for example, nonionic surfactants or aqueous solutions of surfactants or other detergent ingredients. In one preferred embodiment of the invention, perfume is used as the liquid component for promoting the adhesion of the powdering materials.

The nongranulated, partly granulated or completely granulated premix is introduced into the die, the filling level and hence the weight and shape of the tablet formed being determined by the position of the lower punch and the shape of the die. Uniform metering, even at high tablet throughputs, is preferably achieved by volumetric metering of the premix. As the tableting process continues, the top punch comes into contact with the premix and continues descending towards the bottom punch. During this compaction phase, the particles of the premix are pressed closer together, the void volume in the filling between the punches continuously diminishing. The plastic deformation phase in which the particles coalesce and form the tablet begins from a certain position of the top punch (and hence from a certain pressure on the premix). Depending on the physical properties of the premix, its constituent particles are also partly crushed, the premix sintering at even higher pressures. As the tableting rate increases, i.e. at high throughputs, the elastic deformation phase becomes increasingly shorter so that the tablets formed can have more or less large voids. In the final step of the tableting process, the tablet is forced from the die by the bottom punch and carried away by following conveyors. At this stage, only the weight of the tablet is definitively established because the tablets can still change shape and size as a result of physical processes (re-elongation, crystallographic effects, cooling, etc.).

Tabletting machines

The tabletting process is carried out in commercially available tablet presses which, in principle, may be equipped with single or double punches. In the latter case, not only is the top punch used to build up pressure, the bottom punch also moves towards the top punch during the tabletting process while the top punch presses downwards. For small production volumes, it is preferred to use eccentric tablet presses in which the punch(es) is/are fixed to an eccentric disc which, in turn, is mounted on a shaft rotating at a certain speed. The movement of these punches is comparable with the operation of a conventional four-stroke engine. Tabletting can be carried out with a top punch and a bottom punch, although several punches can also be fixed to a single eccentric disc, in which case the number of die bores is correspondingly increased. The throughputs of eccentric presses vary according to type from a few hundred to at most 3,000 tablets per hour.

For larger throughputs, rotary tablet presses are generally used. In rotary tablet presses, a relatively large number of dies is arranged in a circle on a so-called die table. The number of dies varies – according to model – between 6 and 55, although even larger dies are commercially available. Top and bottom punches are associated with each die on the die table, the tabletting pressures again being actively built up not only by the top punch or bottom punch, but also by both punches. The die table and the punches move about a common vertical axis, the punches being brought into the filling, compaction, plastic deformation and ejection positions by means of curved guide rails. At those places where the punches have to be raised or lowered to a particularly significant extent (filling, compaction, ejection), these curved guide rails are supported by additional push-down members, pull-down rails and ejection paths. The die is filled from a rigidly arranged feed unit, the so-called filling shoe, which is

connected to a storage container for the compound. The pressure applied to the premix can be individually adjusted through the tools for the top and bottom punches, pressure being built up by the rolling of the punch shank heads past adjustable pressure rollers.

- 5 To increase throughput, rotary presses can also be equipped with two filling shoes so that only half a circle has to be negotiated to produce a tablet. To produce two-layer or multiple-layer tablets, several filling shoes are arranged one behind the other without the lightly compacted first layer being ejected before further filling. Given suitable process control, shell
10 and bull's-eye tablets – which have a structure resembling an onion skin – can also be produced in this way. In the case of bull's-eye tablets, the upper surface of the core or rather the core layers is not covered and thus remains visible. Rotary tablet presses can also be equipped with single or multiple punches so that, for example, an outer circle with 50 bores and an
15 inner circle with 35 bores can be simultaneously used for tableting. Modern rotary tablet presses have throughputs of more than one million tablets per hour.

- Tableting machines suitable for step a) of the process according to the invention can be obtained, for example, from the following companies:
20 Apparatebau Holzwarth GbR, Asperg, Wilhelm Fette GmbH, Schwarzenbek, Hofer GmbH, Weil, KILIAN, Cologne, KOMAGE, Kell am See, KORSCH Pressen GmbH, Berlin, Mapag Maschinenbau AG, Bern (Switzerland) and Courtoy N.V., Halle (BE/LU). One example of a particularly suitable tableting machine is the model HPF 630 hydraulic
25 double-pressure press manufactured by LAEIS, D.

Three-dimensional form

The cleaning tablets can be made in certain shapes and certain sizes and may also consist of several phases, i.e. layers, inclusions or

cores and rings or shapes with cavities and cavity fillings or inserts. Suitable shapes are virtually any easy-to-handle shapes, for example slabs, bars, cubes, squares and corresponding shapes with flat sides and, in particular, cylindrical forms of circular or oval cross-section. This last
5 embodiment encompasses shapes from tablets to compact cylinders with a height-to-diameter ratio of more than 1.

At a very early stage, developers of tablet-form products came up with the idea of releasing certain ingredients into the wash cycle under defined conditions through differently composed parts or regions of the
10 tablets in order in this way to improve the outcome of the cleaning process. Besides the core/jacket tablets and ring/core tablets known for some time in the pharmaceutical industry, multilayer tablets in particular have been successfully used and are now available for many aspects of washing and cleaning or hygiene.

15 In one particular embodiment of the invention, the cleaning tablet consists of two or more different phases, preferably two or three phases, more preferably two phases, in the form of layers and/or inclusions and/or cores and rings and/or three-dimensional forms with cavities and cavity filling or inserts. The difference between the phases may lie in their
20 composition, for example through the separation of incompatible ingredients, such as bleaching agents and enzymes, and/or different coloring, and/or in their character, for example compressed and non-compressed, for example molten/cast, phases. In one preferred embodiment as a two-phase, more particularly two-layer, cleaning tablet,
25 the two phases are present in a ratio by weight of 10:1 to 1:10, preferably 5:1 to 1:2 and more preferably 3:1 to 1:1.15, for example 2:1 or 1:1.

The portioned pressings may be formed as separate individual elements which correspond to a predetermined dose of the detergent. However, it is also possible to form pressings which combine several such

units in a single pressing, smaller portioned units being easy to break off in particular through the provision of predetermined weak spots. For the use of laundry detergents in machines of the standard European type with horizontally arranged mechanics, it can be of advantage to produce the
5 portioned pressings as cylindrical or square tablets, preferably with a diameter-to-height ratio of about 0.5:2 to 2:0.5. Commercially available hydraulic presses, eccentric presses and rotary presses are particularly suitable for the production of pressings such as these.

The three-dimensional form of another embodiment of the tablets is
10 adapted in its dimensions to the dispensing compartment of commercially available domestic washing machines, so that the tablets can be introduced directly, i.e. without a dosing aid, into the dispensing compartment where they dissolve on contact with water. The cleaning tablets may of course also be used in conjunction with a dosing aid.

15 Another preferred tablet which can be produced has a plate-like or slab-like structure with alternately thick long segments and thin short segments, so that individual segments can be broken off from this "bar" at the predetermined weak spots, which the short thin segments represent, and introduced into the machine. This "bar" principle can also be
20 embodied in other geometric forms, for example vertical triangles which are only joined to one another at one of their longitudinal sides.

Another preferred multiphase tablet which can be produced has a plate-like or slab-like structure with alternately thick long segments and thin short segments, so that individual segments can be broken off from this
25 "bar" at the predetermined weak spots, which the short thin segments represent, and introduced into the machine. This "bar" principle can also be embodied in other geometric forms, for example vertical triangles which are only joined to one another at one of their longitudinal sides. In this case, it is appropriate for optical reasons to make the base of the triangle,

by which the individual segments are interconnected, as one phase while the apex forms the second phase. In this embodiment, different coloring of the two phases is particularly attractive.

In another possible embodiment, however, the various components
5 are not compressed to form a single tablet, instead the tablets obtained comprise several layers, i.e. at least two layers. These various layers may have different dissolving rates. This can provide the tablets with favorable performance properties. If, for example, the tablets contain components which adversely affect one another, one component may be integrated in
10 the more quickly dissolving layer while the other component may be incorporated in a more slowly dissolving layer so that the first component can already have reacted off by the time the second component dissolves. The various layers of the tablets can be arranged in the form of a stack, in which case the inner layer(s) dissolve at the edges of the tablet before the
15 outer layers have completely dissolved. Alternatively, however, the inner layer(s) may also be completely surrounded by the layers lying further to the outside which prevents constituents of the inner layer(s) from dissolving prematurely.

In another preferred embodiment of the invention, a tablet consists
20 of at least three layers, i.e. two outer layers and at least one inner layer, a peroxy bleaching agent being present in at least one of the inner layers whereas, in the case of the stack-like tablet, the two outer layers and, in the case of the envelope-like tablet, the outermost layers are free from peroxy bleaching agent. In another possible embodiment, peroxy bleaching agent
25 and any bleach activators or bleach catalysts present and/or enzymes may be spatially separated from one another in one and the same tablet. Multilayer tablets such as these have the advantage that they can be used not only via a dispensing compartment or via a dosing unit which is added to the wash liquor, instead it is also possible in cases such as these to

introduce the shaped body into the machine in direct contact with the fabrics without any danger of spotting by bleaching agent or the like.

Coating

5 Similar effects can also be obtained by coating individual constituents of the cleaning composition to be compressed or the tablet as a whole. To this end, the mixtures or tablets to be coated may be sprayed, for example, with aqueous solutions or emulsions or melts (spraying on of the coating material) or a coating may be obtained by the process known
10 as melt coating (dipping of the tablet into the melt or solution). In preferred embodiments of the present invention, however, the cleaning tablets are not provided with a coating which covers the entire tablet.

Fracture resistance

15 After pressing, the cleaning tablets have high stability. The fracture resistance of cylindrical tablets can be determined via the diametral fracture stress. This in turn can be determined in accordance with the following equation:

$$\sigma = \frac{2P}{\pi Dt}$$

where σ represents the diametral fracture stress (DFS) in Pa, P is the force in N which leads to the pressure applied to the tablet that results in fracture thereof, D is the diameter of the tablet in meters and t is its height.

Relative equilibrium moisture

Irrespective of the purpose for which they are to be used, the cleaning tablets according to the invention preferably have an equilibrium moisture content of less than 30% at 35°C.

The relative equilibrium moisture content of the cleaning tablets may be determined by standard methods. The following procedure was selected for the present investigations: a water-impermeable 1-liter vessel with a cover having a closable opening for the insertion of samples was
5 filled with a total of 300 g of cleaning tablets and kept at a constant temperature of 23°C for 24 hours in order to guarantee the vessel and the substance a uniform temperature. The water vapor pressure in the space above the tablets can then be determined with a hygrometer (Hygrotest 6100, Testoterm Ltd., England). The water vapor pressure is measured
10 every 10 minutes until two successive values show no deviation (equilibrium moisture content). The hygrometer mentioned above enables the values recorded to be directly displayed in % relative moisture.

Pack

15 The tablets according to the invention may be combined with a pack either individually or two or more at a time. The term "pack" in the context of the present invention always characterizes the primary pack of the tablets, i.e. the pack which is in direct contact with the surface of the tablets on its inside.

20 The tablet/pack combinations according to the invention may of course themselves be packed in secondary packs, for example cardboard boxes or trays, the secondary pack having to meet no other requirements so that any of the usual materials and systems may be used. Accordingly, the secondary pack is possible and normal for institutional applications, but
25 is not necessary.

Water vapor transmission rate

The pack of the tablet(s)/pack combination preferably has a water vapor transmission rate of 0.1 g/m²/day to less than 20 g/m²/day when the

pack is stored at 23°C/85% relative equilibrium humidity. The temperature and humidity conditions mentioned are the test conditions specified in DIN 53122, according to which minimal deviations are acceptable ($23 \pm 1^\circ\text{C}$, $85 \pm 2\%$ relative humidity). The water vapor transmission rate of a given pack or material can be determined by other standard methods and is also described, for example, in ASTM Standard E-96-53T ("Test for Measuring Water Vapor Transmission of Materials in Sheet Form") and in TAPPI standard T464 m-45 ("Water Vapor Permeability of Sheet Materials at High Temperatures and Humidity"). The measurement principle of standard methods is based on the water absorption of anhydrous calcium chloride which is stored in a container in the corresponding atmosphere, the container being closed on top by the material to be tested. The water vapor transmission rate can be calculated from the surface of the container closed by the material to be tested (permeation surface), the increase in weight of the calcium chloride and the exposure time in accordance with the following equation:

$$\text{WVTR} = \frac{24 \cdot 10000}{A} \cdot \frac{x}{y} \quad [\text{g} / \text{m}^2 / 24\text{h}]$$

where A is the surface area of the material to be tested in cm^2 , x is the increase in weight of the calcium chloride in g and y is the exposure time in h.

The relative equilibrium humidity, often referred to as "relative air humidity", in the measurement of the water vapor transmission rate for the purposes of the present invention is 85% at 23°C. The absorption capacity of air for water vapor increases with temperature to a particular maximum content, the so-called saturation content, and is expressed in g/m^3 . For example, 1 m^3 of air at 17°C is saturated with 14.4 g of water vapor, the

saturation content at 11°C being as low as 10 g of water vapor. The relative air humidity is the ratio expressed in percent between the water vapor content actually present and the saturation content corresponding to the prevailing temperature. If, for example, air at 17°C contains 12 g/m³ water vapor, the relative air humidity is $(12/14.4) \cdot 100 = 83\%$. If this air is cooled, saturation (100% relative humidity) is reached at the so-called dew point (in the example 14°C), i.e. a deposit in the form of mist (dew) is formed with further cooling. Hygrometers and psychrometers are used for the quantitative determination of humidity.

10 The relative equilibrium humidity of 85% at 23°C can be adjusted to an accuracy of $\pm 2\%$ relative humidity (depending on the instrument used), for example in humidity-controlled laboratory chambers. Oversaturated solutions of certain salts also form constant and well-defined relative air humidities at a given temperature in closed systems, these relative air
15 humidities being based on the phase equilibrium between the partial pressure of the water, the saturated solution and the sediment.

Accordingly, the present invention also relates to a combination of (a) cleaning tablet(s) containing polyalkylene glycol and a pack containing the cleaning tablet(s), the pack having a water vapor transmission rate of
20 0.1 g/m²/day to less than 20 g/m²/day where the pack is stored at 23°C/85% relative equilibrium humidity.

According to the invention, preferred packs have a water vapor transmission rate of 0.5 g/m²/day to less than 15 g/m²/day.

25 *Dose*

The pack surrounds one or more cleaning tablets, depending on the embodiment of the invention. In one preferred embodiment of the invention, a tablet may be made up in such a way that it constitutes a dosage unit of the cleaner/detergent and may be individually packed or

tablets may be packed in a pack in numbers which, together, constitute a dosage unit.

“Individually packed” does not mean that the tablets have to be accommodated in physically separated packs, instead a tablet can be removed from the pack without the other individually packed tablet(s) present in the pack also having to be taken out. A corresponding individual pack is, for example, the blister pack described in the following Examples. The same applies to the pack unit containing more than one tablet which may of course be part of a physical combination of several pack units providing each pack unit can be individually opened while the others remain closed.

Accordingly, for a prescribed dose of 80 g of detergent/cleaner, which is typical of laundry detergents, it is possible in accordance with the invention to produce and individually pack a detergent tablet weighing 80 g. However, it is also possible in accordance with the invention to pack two detergent tablets each weighing 40 g as a dosage unit in one pack in order to obtain a combination according to the invention. This principle may of course also be extended so that, according to the invention, combinations of three, four, five or even more cleaning tablets may be accommodated in one and the same pack.

Two or more tablets in the same pack may of course have different compositions. In this way, certain components can be spatially separated from one another in order, for example, to avoid stability problems.

25 *Material and form*

The pack may consist of various materials and may assume various external forms. For economic reasons and in the interests of easier processability, however, preferred packs are those in which the packaging material is light in weight, easy to process and inexpensive.

In preferred combinations according to the invention, more particularly combinations with cleannig tablets, the pack consists of a body with one or more depressions for accommodating one or more tablets and a cover closing the depression and holding the tablet(s) therein. Packs
5 such as these are known as blister packs. The body is preferably made of transparent or nontransparent plastic film, more particularly polypropylene film, with a thickness of preferably 200 to 600 μm and more particularly 300 to 500 μm , for example 400 μm . The cover is normally a preferably
10 welded-on film of metal, plastic, metal-coated plastic or paper or wax-coated paper with a thickness of preferably 60 to 200 μm and more particularly 100 to 140 μm , for example 120 μm . Suitable cover films are the commercially available peel, peel-and-push and push-through films widely used above all in the pharmaceutical industry. A pack of the type in question is described in the following Examples and in **EP 0 903 405 A2**
15 (*Unilever*) to which reference is made in this regard and of which the disclosure is hereby incorporated in the present specification.

In other preferred combinations according to the invention, more particularly combinations with laundry and dishwasher detergent tablets, the pack consists of a bag of single-layer or laminated paper and/or plastic
20 film. The cleaning tablets may be introduced without sorting, i.e. loosely, into a bag of the materials mentioned above. However, for aesthetic reasons and for sorting the combinations in secondary packs, bags are filled either with single cleaning tablets or with several cleaning tablets in sorted form. The term "flow pack" is now commonly used for individual
25 dosage units of the cleaning tablets accommodated in a bag. Flow packs may optionally be packed - again preferably sorted - in outer packs which underscores the compact supply form of detergent tablets. The bags of single-layer or laminated paper or plastic film preferably used as the pack may be designed in various ways, for example as inflated bags with no

center seam or as bags with a center seam which are closed by heat (heat sealing), adhesives or adhesive tape. Single-layer bag materials are the known papers, which may optionally be impregnated, and plastic films which may optionally be co-extruded. Plastic films which may be used as
5 packs in accordance with the invention are described, for example, in **Hans Domininghaus "Die Kunststoffe und ihre Eigenschaften" 3rd Edition, VDI Verlag, Düsseldorf, 1988, page 193**. Figure 111 of this publication also provides reference points in respect of the water vapor transmission of the materials mentioned. Particularly preferred combinations according to
10 the invention contain a bag of single-layer or laminated plastic film with a thickness of 10 to 200 μm , preferably 20 to 100 μm and more preferably 25 to 50 μm as the pack.

Although wax-coated papers in the form of paperboard articles may also be used in addition to the films or papers mentioned as the pack for
15 the cleaning, the pack preferably does not comprise any boxes of wax-coated paper.

Examples

Cleaning tablets **E1** to **E9** according to the invention and comparison
20 tablets **C1** and **C2** were produced as described above in the form of circular disks weighing 25 g with a density of about 1.8 g/cm³ and were tested for moisture stability. Their compositions are shown in Tables 1 and 2 below along with their dissolving times and lime dissolving power.

In terms of composition and size, the cleaning tablets according to
25 the invention represent an embodiment suitable for use as lavatory cleaners. The tablets in Table 1 are lavatory cleaner tablets based on amidosulfuric acid with and without additions of 1 or 5% by weight of polyethylene glycol having a molecular weight of 10,000 (PEG 10000), tablets **E1**, **E2** and **C1** being distinguished by high effervescent activity and

foaming and tablets **E3**, **E4** and **C2** by reduced effervescent activity and foaming.

Table 1

% by weight	E1	E2	C1	E3	E4	C2
PEG 10000	1	5	-	1	5	-
Amidosulfuric acid	60	60	60	60	60	60
Citric acid	5	5	5	5	5	5
Sodium carbonate	5.48	5.48	5.48	18	12	18
Sodium bicarbonate	24	20	25	-	-	-
Sodium lauryl sulfate	0.9	0.9	0.9	0.9	0.9	0.9
Sodium perborate·1H ₂ O	2	2	2	2	2	2
Sodium sulfate	-	-	-	11.48	13.48	12.48
Polyvinyl pyrrolidone	0.5	0.5	0.5	0.5	0.5	0.5
Paraffin oil	0.6	0.6	0.6	0.6	0.6	0.6
Silicon dioxide	0.1	0.1	0.1	0.1	0.1	0.1
Perfume	0.4	0.4	0.4	0.4	0.4	0.4
Dye	0.02	0.02	0.02	0.02	0.02	0.02
Lime dissolving power [mg]	1337	1366	1357	1309	1271	1320
Dissolving time [mins.]	6.5	9.5	6	8	8	7

Tablet **E5** is based on citric acid and contains about 2.2% by weight of PEG 3350. Tablet **E6** is based on sodium hydrogen sulfate and contains 0.5% by weight of PEG 6000 and inter alia sodium percarbonate. Tablet **E7** is based on a 1:1 mixture of amidosulfuric and citric acid and contains 2% by weight of PEG 10000. Tablet **E8** is based on amidosulfuric acid and contains 5% by weight of PEG 3350 and inter alia sodium percarbonate and tripolyphosphate, but no polyvinyl pyrrolidone.

Table 2

% by weight	E5	E6	E7	E8	E9	
					Phase 1	Phase 2
PEG 10000	-	-	2	-	1	1
PEG 6000	-	0.5	-	-	-	-
PEG 3350	2.195	-	-	5	-	-
Amidosulfuric acid	-	-	32	60	65	50
Citric acid	65	-	32	5.48	5	5
Sodium hydrogen sulfate	-	64	-	-	-	-
Sodium carbonate	30	25	6	21	14	18
Sodium bicarbonate	-	-	26.5	-	-	-
Sodium lauryl sulfate	0.1	0.9	0.5	0.3	0.9	0.9
Magnesium stearate	2	2.5	-	-	-	-
Sodium percarbonate	-	1	-	2	-	4
Sodium tripolyphosphate	-	-	-	6	-	-
Sodium sulfate	-	4.5	-	-	12.48	19.48
Polyvinyl pyrrolidone	0.5	0.7	0.5	-	0.5	0.5
Paraffin oil	-	0.5	-	-	0.6	0.6
Silicon dioxide	-	-	0.18	-	0.1	0.1
Perfume	0.2	0.4	0.3	0.2	0.4	0.4
Dye	0.005	-	0.02	0.02	0.02	0.02
Lime dissolving power [mg]	805	886	911	1087	1380	
Dissolving time [mins.]	7	8.5	5	4.5	9	

- Tablet **E9** is a two-phase cleaning tablet which consists of two layers in the form of circular disks with the same weight and the phase 1 and phase 2 compositions shown in Table 2, of which only phase 2 contains bleaching agent. Both phases are based on amidosulfuric acid and contain 1% by weight of PEG 10000. However, phase 1 has a larger amidosulfuric acid content while phase 2 has a larger sodium carbonate content and additionally contains sodium percarbonate.

Lime dissolving power

The dissolving power for limescale (calcium carbonate) was determined as follows.

5 The test was carried out on a plate of white Carrara marble measuring 75 x 150 x 5 mm. Before the tests, the marble plates were degreased with ethanol and any residues were brushed off under running water. The plate was then dried for at least 1 hour at 105°C to constant weight and, after cooling, was weighed on an analytical balance (accuracy
10 ± 1 mg).

Of 8 tablets, 1 liter of a 20% solution was prepared with tap water. The tablets were dissolved by stirring for 10 minutes at room temperature.

950 ml of the cleaning solution were transferred to a 1 liter glass beaker (tall form). Before the beginning of the test, the temperature of the
15 cleaning solution was checked to ensure a value of 20 to 23°C. The immersion time was 10 minutes. The test plate was then removed, residues were brushed off under running water and the plate was again dried at 105°C to constant weight. The quantity of dissolved calcium carbonate was determined by differential weighing and is shown in the
20 Tables as the lime dissolving power in mg.

The tablets according to the invention and the comparison tablets based on amidosulfuric acid showed comparable lime dissolving power. As expected, the lime dissolving power of tablets **E5** to **E7** with the alternative acid base was lower commensurate with to the particular acid component.

25

Dissolving time

The dissolving time of a tablet is the time which the tablet takes to visibly dissolve completely in the standing water volume (1 liter) of the U pipe of a conventional flush toilet on its own, i.e. without any mechanical

assistance, for example in the form of a stirrer.

The tablets according to the invention and the comparison tablets showed comparable dissolving times.

5 Moisture stability

Moisture stability was tested in a commercially available pack. 8 tablets were accommodated in individual cells of a polypropylene blister pack which, before thermoforming, had a thickness of 400 µm. The blister pack was closed by a welded-on peel and push film (wall thickness 120
10 µm) as the cover film.

The packed tablets were stored under different conditions I and II.

Storage I at 80% relative humidity

The tablets were stored for 4 weeks at a temperature of 30°C/80%
15 relative air humidity.

Storage II at more than 80% relative humidity

The tablets were stored for 2 months at a temperature of 23°C and in a saturated moisture atmosphere of more than 80% relative humidity. To
20 this end, the pack was stored in a screw-top 2-liter wide-necked bottle containing an open 250 ml glass filled with 100 ml of water.

Moisture stressing of the tablets

To determine the moisture stressing of the packed tablets, the pack
25 was filled with 6 g of the drying agent silica gel per cell and stored for 21 days at 23 and 30°C in a storage II arrangement.

At 23°C, 224 mg of water were taken up over a period of 21 days; at 30°C, the figure was 938 mg water. Accordingly, each tablet is exposed daily in the pack to a quantity of water of up to about 1.3 mg at a storage

temperature of 23°C and up to about 5.6 mg at a storage temperature of 30°C.

Storage results

5 Tablets **E1** to **E9** according to the invention proved to be moisture-stable. Neither the tablets nor the blister pack showed any visible signs of having changed after storage I and storage II under rigorous moisture conditions. The tablets could be used intact.

10 By contrast, comparison tablets **C1** and **C2** were not moisture-stable. After storage I, tablets **C1** had swollen, changed color and partly reacted with the moisture to form gas, so that the cells of the blister pack had expanded. After storage II, tablets **C1** had again swollen, the cells of the blister pack had expanded and the tablets could no longer be used. Tablets **C2** had changed color and had swollen slightly with some formation
15 of gas in the blister pack both after storage I and after storage II.

 The various test results show that tablets **E1** to **E9** according to the invention were distinguished from comparison tablets **C1** and **C2** by superior moisture stability for comparable lime dissolving power and dissolving time.

20 The invention may be varied in any number of ways as would be apparent to a person skilled in the art and all obvious equivalents and the like are meant to fall within the scope of this description and claims. The description is meant to serve as a guide to interpret the claims and not to limit them unnecessarily.

CLAIMS

1. Cleaning tablets comprising one or more polyalkylene glycols, but excluding
 - i) surfactant and builder particles coated with a polyethylene glycol having
5 a molecular of 1,500;
or which have been produced
 - ii) using 5 to 20% by weight of an amorphous overdried silicate,
 - iii) using 1 to 15% by weight of water or aqueous solutions or
 - iv) by compacting a particulate detergent composition with a binder
10 distributed therein at a temperature of at least 28°C, but below the
melting point of the binder of 35° to 90°C.
2. A tablet as claimed in claim 1, wherein there is present from 0.1 to 20% by weight of one or more polyalkylene glycols.
3. A tablet as claimed in claim 1 or 2, wherein there is present one or
15 more polyalkylene glycols from the group comprising polyethylene glycols, polypropylene glycols, polytetrahydrofurans and copolymers of ethylene oxide, propylene oxide and/or tetrahydrofuran.
4. A tablet as claimed in claims 1, 2 or 3, wherein there is present one or more polyethylene glycols with a molecular weight of at least 3,000.
- 20 5. A tablet as claimed in claim 4, wherein the molecular weight is in the range of from 4,000 to 50,000.
6. A tablet as claimed in claim 4, wherein the molecular weight is in the range of from 6,000 to 40,000.
7. A tablet as claimed in claim 4, wherein the molecular weight is in the
25 range of from 8,000 to 30,000.
8. A tablet as claimed in claim 4, wherein the molecular weight is in the range of from 10,000 to 20,000.
9. A tablet as claimed in any of claims 1 to 8, wherein there is present one or more disintegration aids.

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10. A tablet as claimed in claim 9, wherein the disintegration aid is an effervescent system.
11. A tablet as claimed in claim 9, wherein the disintegration aid is an effervescent system comprising amidosulfuric acid, citric acid and/or sodium hydrogen sulfate in combination with sodium carbonate and/or sodium hydrogen carbonate.
12. A tablet as claimed in any of claims 1 to 11, wherein there is present one or more surfactants.
13. A tablet as claimed in claim 12, wherein there are present one or more anionic surfactants.
14. A tablet as claimed in claim 12, wherein one or more alkyl sulfates are present.
15. A tablet as claimed in any of claims 1 to 14, wherein there is present one or more bleaching agents.
16. A tablet as claimed in claim 15, wherein there is present at least one oxygen bleaching agent selected from the group comprising alkali metal perborates, alkali metal percarbonates, organic peracids and hydrogen peroxide.
17. A tablet as claimed in claim 15, wherein the bleaching agent is selected from the group comprising alkali metal perborates and alkali metal percarbonates.
18. A tablet as claimed in claim 15, wherein the bleaching agent is sodium perborate and/or sodium percarbonate.
19. A tablet as claimed in any of claims 1 to 18, wherein there is present one or more builders.
20. A tablet as claimed in any of claims 1 to 19, wherein there is present one or more other ingredients from the group consisting of corrosion inhibitors, soil release compounds, enzymes, soil repellents, optical brighteners, dyes and perfumes, antimicrobial agents, fillers, release

agents or lubricants, binders, powdering materials and antimicrobial agents.

21. A tablet as claimed in any of claims 1 to 20, wherein the tablet consists of two or more different phases.

5 22. A tablet as claimed in claim 21, wherein the tablet comprises two or three phases.

23. A tablet as claimed in claim 21, wherein the tablet comprises two phases.

24. A process for the production of a cleaning tablet by compacting a
10 particulate cleaning composition with one or more polyalkylene glycols distributed therein at a temperature below 28°C.

25. A combination of one or more cleaning tablets containing polyalkylene glycol and a pack for accommodating the cleaning tablets, the pack having a water vapor transmission rate of 0.1 g/m²/day to less than 20
15 g/m²/day where it is stored at 23°C/85% relative equilibrium humidity.

26. The use of one or more cleaning tablets claimed in any of claims 1 to 24 for cleaning lavatories, descaling, cleaning hard surfaces, manual dishwashing, machine dishwashing, bleaching, stain removal, washing and/or water softening.